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CHEMICAL THEORY.

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A HISTORY

OF

CHEMICAL THEORY

FROM THE AGE OF LAVOISIER TO

THE PRESENT TIME.

BY

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PREFACE.

THE graphic History of Chemical Theory here presented to the English reader, forms the Introductory Discourse to M. Wurtz's 'Dictionnaire de Chimie.' Though the opening sentences may be thought to savour too strongly of national partiality, it will nevertheless be found that the Author has habitually done full justice to the labours of chemists belonging to other nations. One or two discoveries having important bearings on the development of chemical theory have however been passed over, and these the Translator has endeavoured to elucidate by a few additional notes.

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HISTORY

OF

CHEMICAL THEORY

FROM THE TIME OF LAVOISIER.

INTRODUCTION.

CHEMISTRY is a French science. It was founded by Lavoisier, of immortal memory.* For ages, it had been nothing but a collection of obscure receipts, often fallacious, used by the Alchemists, and afterwards by the Iatrochemists. Vainly had a great mind, George Ernest Stahl, endeavoured, at the commencement of the eighteenth century, to give it a scientific foundation. His system could not stand the test of facts or the searching criticism of Lavoisier.

The work of Lavoisier is complex: he was at once the author of a new theory and the creator of the true method in chemistry; and the superiority of the method gave wings to the theory.

* Note A, at the end.

Sprung from exact observation of the phenomena of combustion, this theory was able to embrace all important facts known at that epoch. It had within itself both exactness and scope; it has become a system. After fifteen years of strife, its triumph was complete, and it remained unquestioned for more than half a century: the master found great disciples to consolidate and develop his work. Nevertheless, a part of the science remained beyond the reach of their efforts, and of the system, which was more especially applicable to inorganic compounds. Organic chemistry was at that time limited to the qualitative description of principles extracted from products of vegetable and animal origin. The genius of discovery had indeed amassed a quantity of precious materials; but the science, which was to co-ordinate them, was not yet born. The very elements of this co-ordination were still wanting, and could be furnished only by the study of the metamorphoses of organic compounds. To discover the atomic constitution of organic compounds, and thereby to explain their properties, and establish their relations, is the object of Organic Chemistry; and this object is attained by determining the nature and number of the constituent atoms of organic compounds, and by studying their modes of formation and transformation.

This great work was not really begun till about

the year 1830; but from that time it has been carried on with vigour and success. It is not yet finished. But what a mass of facts has been accumulated during this long space of time! No memory can at present retain them all; and it may be said, without exaggeration, that, since the time of Lavoisier, the wealth of the science has been increased a hundredfold. Hence, the frame in which that great genius enclosed his system has become too narrow. An enlarged horizon reveals new points of view. Is it, then, astonishing that theories suggested by the study of organic compounds, and at first restricted within the domain which gave them birth, have taken wing, and striven to clear the bounds which separate organic from mineral chemistry? This they have done; they now embrace the whole field of the science; and, thanks to them, it may be said that there is but one chemistry.

So great a result is not the work of one day or the conquest of a revolution; it is the result of slow and continued progress. But if we forget for a moment the successive stages, and carry our ideas back to the starting-point, we must avow that the progress is immense. Compared with the science of that time, the science of the present day appears to us not only enlarged, but transformed and regenerated.

Is it complete, as regards its doctrines; and are

the new paths by which it has irresistibly advanced, made altogether plain? We do not think so. But the greatness of the advance permits us to affirm that the roads are good. We may then halt for a moment, and, casting our eyes over the distance already traversed, mark with certainty the point at which we have arrived.

LAVOISIER

I.

The system of Lavoisier has been characterised as antiphlogistic, in opposition to the celebrated theory proposed by Stahl, towards the end of the seventeenth century, and known by the name of 'Theory of Phlogiston.' This great chemist, who was also a great physician, had found the germ of this theory in the writings of Becher.* Metals contain a combustible principle, an 'inflammable earth:' such is the idea of the last-named philosopher, still governed by the belief of the alchemists, whom also he resembled in his restless spirit and adventurous career. But these notions were beginning to decline, and the stamp attached to the doctrines of Becher was no longer a mark of favour. Thus his idea was scarcely noticed in its origin. To bring it out and

* Johann Joachim Becher was born at Speier in 1635, and died in England in 1682. His first ideas on the nature of the metals were published in his *Acta laboratorii chymici Monacensis, seu Physica subterranea*, 1669. He explained them chiefly in his last work, entitled, *Alphabetum minerale, seu viginti-quatuor theses Chymicæ*, 1682.

make it known, it required a powerful commentator, and such a commentator it found in Stahl. 'Becheriana sunt quæ profero' was the declaration of Stahl; and nevertheless the idea became his own. He gave it a clear expression and a general form; he developed it into a theory.*

The inflammable earth of Becher received the name of *Phlogiston*. This, according to Stahl, was a subtle principle, diffused through metals and in general through combustible bodies, which lose it when they are burned or calcined. A metal, heated in the air, gives up its phlogiston, and is at the same time converted into a dull-looking powder, a metallic calx. The sparkling scales detached by the hammer from red-hot iron consist of dephlogisticated iron. The yellow powder called litharge, formed by the prolonged calcination of lead, is lead deprived of its phlogiston. Incombustible bodies are bodies deprived of this principle; inflammable bodies are those which contain it in large quantity. The phenomenon of fire is a powerful disengagement of phlogiston. A

* George Ernest Stahl, born at Anspach in 1660, died in 1734, was principal physician to the King of Prussia. The first in date of his chemical writings, his *Zymotechnia Fundamentalis*, etc., published in 1697, contains, together with an affirmation of the ideas of Becher, the foundation of the phlogistic theory. After having published in 1702 a new edition of Becher's *Physica subterranea*, he developed his ideas chiefly in the following works: *Specimen Becherianum, fundamenta, documenta et experimenta sistens; Experimenta, observationes, animadversiones*, ccc. numero, *Chymicæ et Physicæ* (1731).

body subjected to the action of fire becomes decomposed, and that which remains after the combustion was previously one of the elements of the combustible body. Thus the ashes of metals, or metallic calxes, were contained in the metals themselves in combination with phlogiston. This latter may be restored to them by heating them with substances rich in phlogiston, such as carbon, wood, or oil. Calcine litharge with powdered charcoal, and you will recover metallic lead. The phlogiston will leave the charcoal to unite with the litharge, and form with it the revivified lead.

The triumph of a theory is to embrace the greatest number and the greatest variety of facts. Now the theory of phlogiston was equally applicable to two opposite orders of phenomena, and united them by a theoretical bond. Bringing together the phenomena of combustion, and the facts relating to the calcination of metals in the air, and their conversion into metallic calxes, it explained both the one and the other; and, moreover, gave a very simple interpretation of the phenomena of reduction, the inverse of the former.

But what was the part played by the air in combustion? On this point the theory was mute; and nevertheless observation had gone before it, and had long before directed attention to the importance of this condition of the change. Jean Rey, physician, of Périgord, had caught a glimpse of it as early as

1630. Robert Boyle, the first President of the Royal Society of London, and likewise the first in date of the true chemists, had confirmed the fact previously noticed by Rey, that metals increase in weight when calcined in the air. He added to it this important feature, that the conversion of lead into litharge, in a space containing a limited quantity of air, gives rise to a diminution of the volume of this air. He knew that the air contains a principle which is consumed during respiration and combustion. His contemporary and fellow-countryman, Dr. John Mayow, had suspected, since 1669, that the air is not wholly formed of one and the same substance, but that it contains certain particles, better adapted than the rest for supporting combustion, and that those particles,* removed from the air by burning bodies, are likewise absorbed by the blood in the lungs.

All these observations, however, had remained barren in a theoretical point of view. They were either wholly disregarded, or were set aside by explanations equally superficial and erroneous. The increase in weight of metals by calcination was attributed by Robert Boyle to the heat absorbed. Stahl was acquainted with it, and mentions it without explanation, regarding it, in fact, as a secondary detail.

At this time chemists were exclusively occupied with the outward appearance of facts, confining them-

* *Particulæ nitro-aëreæ.*

selves to the observation and description of what might be called the qualitative side of phenomena. The study of the relations of quantity in chemical reactions was neglected as a luxury, useless for theory, or at all events was altogether disregarded in relation to it.*

II.

A NEW era opens with Lavoisier. The facts relating to the increase in weight of metals during combustion, confirmed by him, multiplied by a series of decisive experiments, and illuminated by a lucid discussion, become in his hands at once a victorious arm against the theory of phlogiston, and the corner-stone of a new system. Combustion is not a decomposition; it is a combination, resulting from the fixation of a certain element of the air on the burning body. The latter increases in weight in the act of consuming, and this increase of weight represents exactly the weight of the gaseous body added.

The discovery of the gas eminently adapted for supporting combustion, made by Priestley in 1774, gave a new force to this theory. Lavoisier showed that this gas is one of the elements of the air, and called it *oxygen*. From this time the part played by the air in the phenomena of combustion was clearly established. In vain did the last defenders of phlo-

* Note B, at the end.

giston, Cavendish, Priestley, the great Scheele himself, endeavour to save the theory of Stahl by modifying it, and asserting that the function of the air consists in removing phlogiston from combustible bodies. 'A gas,' said Priestley, 'is so much the better adapted for supporting combustion, as it contains within itself a smaller quantity of phlogiston; the air contains but little of it; the gaseous constituent of the air, which is pre-eminently a supporter of combustion, contains none: the other element of the air is saturated with it, and is therefore incapable of supporting combustion.' These reasonings, which represented an incombustible gas (nitrogen), as rich in phlogiston, disfigured the theory instead of saving it. Lavoisier victoriously opposed to them an argument drawn from relations of weight. 'The whole,' said he, 'is greater than its part: the products of combustion, which are heavier than the combustible bodies, cannot therefore be the elements of the latter, for in chemical reactions nothing is lost, nothing is created, matter being indestructible. If bodies increase in weight by burning, it is by the gain or addition of a new substance; when, on the other hand, metallic calxes or oxides are reduced to the metallic state, the effect is due, not to the restitution of phlogiston, but to the loss of the oxygen which they contain.' It was thus that Lavoisier first established the elementary nature of the metals, and fixed in general the notions of

simple bodies. He recognised as such those bodies which yield only one kind of matter, and, when submitted to the action of all available forces, remain constantly the same, indestructible, undecomposible. Having thus impressed on a large number of primordial substances the seal of a peculiar individuality, he finally recast the ancient notions on the nature of elements, and put an end to the hope of effecting transmutations. This secular illusion, neither encouraged nor destroyed by the partisans of phlogiston, might indeed be expected to last as long as the metals were regarded in the light of compound bodies.

The elementary bodies thus defined are represented by Lavoisier as endowed with the power of uniting together, so as to form compound bodies, this union taking place without loss of substance, and in such a manner that all the ponderable matter of the constituent bodies is found in the compound. These great principles form the basis of chemistry. Now that they are universally adopted, they appear to us so simple and indisputable that we feel compelled as it were to admit them as axioms. But they were not so at the time in question; and it is the lasting glory of Lavoisier to have proclaimed and moreover demonstrated them. This he has done by a series of researches strongly bound together by one dominant idea, and rendered immortal by skill in experiment, clearness of exposition, and rigorous exactness of

deduction. And if anything could vie in importance with the discoveries of the great master, it would be his method, that method which consists in applying the balance to all chemical phenomena, and is his own, because he was its true promoter. Cavendish, Bergmann, Margraf, had made quantitative analyses, but neither of them had thought of applying the study of ponderal relations to the solution of a theoretical question.* This idea and this merit are due to Lavoisier. The method which he inaugurated is the only true method of chemical research. Not only has it not been replaced by any other, but we cannot even conceive the possibility of such replacement.

Having taken as his starting-point the study of the phenomena of oxidation, Lavoisier naturally bestowed the greatest amount of attention on oxygen and the compounds which contain it. He showed the important part played by this gas in the formation of acids and salts. The principles which guided him in the study of oxygenated compounds, the most important of all, were easily extended to all other chemical compounds. Hence there resulted a general theory, which about the year 1775 was put forward in opposition to the ideas of Stahl, then prevailing. The strife was keen, and even those who, after Lavoisier, mainly contributed to overturn the phlogistic theories by their discoveries, were nevertheless to

* Note B, at the end.

the end its most determined champions. Scheele died in 1784, at the age of 83, if not a fully convinced partisan of the idea of phlogiston in the sense attached to it by Stahl, at all events an energetic defender of the word: so true is it that habit is our master. In the same year, 1784, when the new doctrine had mastered all enlightened minds in France, with Berthollet at their head, Cavendish published an elaborate and ingenious defence of the phlogistic theory. Subsequently he withdrew his opposition, though without actually surrendering. Priestley never ceased to oppose the new theory. He died in 1804, near the sources of the Susquehannah, having carried into the new world his restless spirit and his obstinacy. As to Lavoisier, cut off in the flower of his age and the fulness of his activity, he had the satisfaction, rare for so great an innovator, of finally witnessing the triumph of his ideas. In 1794, on the day when the revolutionary axe put an end to his existence, his theory had been accepted by the greater number of men competent to judge, and the few opponents who still dared to raise their voice, could not retard the fall of a system already condemned.

III.

Having in the preceding pages sketched in broad lines the work of Lavoisier, we must now enter upon

a few details, and trace the development of his doctrines consequent upon the discoveries which belong to him or to his successors.

In 1772 Lavoisier deposited at the Academy a sealed packet. He therein treats for the first time of the increase in weight which metals acquire by calcination. He further shows that sulphur and phosphorus increase in weight when they burn in the air, and that this increase of weight is due to the absorption of a certain quantity of air. Lastly, he shows that the reduction of metallic calxes gives rise to a disengagement of air.

Some of these experiments are described in detail in a memoir published in 1774. Having kept tin for a long time in the state of fusion in a close vessel, Lavoisier observed, as indeed Black had done before him, a diminution in the volume of the air. But, more sagacious and skilful than his predecessor, he was able to establish the fact, that the increase in weight of the tin represents exactly the weight of the air which enters the vessel when it is opened after cooling. This observation amounted to showing that the tin increases in weight because it has absorbed air: for the air which disappears from the vessel by absorption evidently weighs as much as that which replaces it in equal volume at the end of the experiment.

Shortly after the discovery of oxygen by Priestley,

in 1774, Lavoisier published a new memoir, in which he shows that, in the calcination of metals and in combustion, it is not the whole of the air, but one of its elements, namely, oxygen, that is absorbed. He at first calls this constituent *vital air*, or *air eminently adapted for supporting combustion and respiration.* In preparing this gas, as Priestley had done, by the calcination of mercurial calx, he shows that the latter is a compound of mercury and oxygen, and concludes, by analogy, that all metallic calxes have a similar composition. He represents them as formed of metal and vital air (oxygen).

Starting from the fact, already known in his time, that metallic calxes, when heated with charcoal, are converted into metal, at the same time that fixed air (carbonic acid) is evolved, Lavoisier regards the latter as a compound of charcoal and vital air. He likewise concludes that this vital air is one of the elements of saltpetre, which supports so vividly the combustion of charcoal, giving off fixed air. The composition of this latter gas was soon afterwards established by a brilliant synthesis. Having effected the combustion of the diamond, for the first time since the famous experiment of the Academicians *del Cimento*, Lavoisier showed that the sole product of this combustion is fixed air, designated from that time as carbonic acid.

Thus inaugurated, his researches on the composi-

tion of acids were continued in 1777 by the examination of phosphoric acid produced by the combustion of phosphorus. After having again shown that this latter body increases in weight by burning, Lavoisier determines exactly the function of the air in the phenomenon, by showing that the fifth part of this air is absorbed by the phosphorus.

Other experiments, undertaken in the same year, strengthen the conclusion that of the two elements of the air, one only, namely, oxygen, is capable of supporting combustion.

His researches on the composition of sulphuric acid are related to the preceding. He shows that this acid differs from sulphurous gas by containing a larger proportion of oxygen. He points out the same relations of composition between nitric acid and the gaseous oxide of nitrogen discovered just before by Scheele, and indicates, as a compound intermediate between these two bodies, the ruddy vapour produced by the direct oxidation of oxide of nitrogen. All these researches demonstrate the part played in the formation of acids by this 'air eminently adapted for supporting combustion and respiration,' which, in a memoir published in 1778, he for the first time calls *oxygen*.

Afterwards he returns to oxides, and passes on to salts. Having endeavoured to determine the proportions in which oxygen combines with metals, he

represents oxides as essential constituents of all salts. Before his time, the constitution of these latter bodies was generally misunderstood. They were represented, sometimes as formed by an acid united to a metal, sometimes as resulting from the union of a metallic calx with an acid, the facts then known being invoked by turns for the support of one or the other of these views. It was known that litharge is capable of forming a salt by dissolving in vinegar; but a large number of salts were also known to be formed by the action of an acid upon a metal. Is not white vitriol or zinc sulphate formed when the metal zinc is wetted with dilute sulphuric acid? The disengagement of hydrogen which accompanies this solution, disregarded at first, afterwards received a false interpretation. Lavoisier showed that this hydrogen proceeds from the decomposition of the water which takes part in the reaction, and the oxygen of which is fixed upon the zinc. It is not, therefore zinc, but oxidised zinc, or oxide of zinc, which combines with the sulphuric acid.

The action is different, but the results are analogous when copper dissolves in nitric acid. In this case, the metal exerts a decomposing action, not on the water, which is always present, but on a portion of the acid itself, which gives up oxygen to it. The copper is thus converted into oxide, which unites with another portion of the nitric acid to form a salt.

With regard to the portion of acid which has yielded oxygen to the metal, it is brought, by this deoxidation or reduction, to the state of ruddy vapour or hyponitric acid, which escapes.

Such is the interpretation given by Lavoisier to the phenomena of the solution of metals in acids, phenomena whose diversity had embarrassed his predecessors, and whose meaning had escaped them. The great reformer refers them to this double mode of action: preliminary oxidation of the metal; combination of the oxide thus formed with the acid.

Having thus recognised the part played by oxygen in the formation of acids, oxides, and salts, he laid, by a few very simple definitions, the foundations of a new system of chemistry.

An acid results from the union of a simple body, generally non-metallic, with oxygen.

An oxide is a combination of metal and oxygen.

A salt is formed by the union of an acid with an oxide.

These principles, demonstrated with regard to oxygen compounds, were capable of immediate extension to other chemical compounds.

A sulphide results from a combination of sulphur with a metal.

A phosphide contains a metal together with phosphorus.

The chlorides alone still remained, if not external

to the system, at all events beyond the reach of exact definition. In fact, chlorine having been regarded by Berthollet as a compound of muriatic acid and oxygen, the chlorides were included for a long time among oxygenated compounds. But this error, which was afterwards corrected, could not invalidate the new theory, which represented simple bodies as endowed with a power of combining together without loss of substance, and forming compounds of various orders according to their degree of complexity.

An elementary body combines with another elementary body, whence there results a compound of the first order. Acids, oxides, sulphides, &c. belong to this order of combination, which is the simplest of all.

But the acids and oxides themselves are endowed with the power of combining one with the other, to form binary compounds of the second order, which are salts.

Whatever may be the degree of complexity of a compound, we may always discern in it two constituent parts, or proximate elements, which may themselves be either simple or compound. Sulphide of iron contains two constituent parts, sulphur and iron—both elementary bodies. In green vitriol a new elementary body is added to the preceding; this salt contains, in fact, sulphur, iron, and oxygen; but these elements are combined in it in such a manner,

that the oxygen is divided between the sulphur and the iron, producing sulphuric acid with the former, and oxide of iron with the latter. This acid and this oxide are the proximate elements of the salt.

Thus all chemical compounds are binary: such is the essential character of the system. In all combinations, the affinity is exerted upon two elements, simple or compound. These attract one another, and unite together by virtue of a certain opposition of properties, which is neutralised by the act of union. Such is dualism.

It is the foundation of the theory and the principle of the language of chemistry. And this language, so admirable for its precision, contributed in no slight degree to the triumph of the ideas, at the end of the last century.

IV.

There was then, at the Parliament of Dijon, an 'Avocat Général' named Guyton de Morveau, who nobly devoted his leisure hours to the study of chemistry and mineralogy. He had been struck, in public lectures, with the inconveniences of the nomenclature, if that term could be properly applied to a language destitute of method and clearness—a mere collection of uncouth words and tiresome synonymes. Already, in 1782, he had suggested new

names, which were not accepted, though they contained the germ of a new nomenclature.

To designate the composition of a substance by its very name—such was the end of the reform undertaken by Guyton de Morveau.

It found a powerful supporter in Lavoisier, who, for his own part, succeeded in gaining over to the new doctrine the author of the nomenclature. A mutual understanding was thus established in 1787, and, thanks to the preponderating influence of Lavoisier, and to the assistance of Berthollet and Fourcroy, the new language was made to adapt itself to the new theory.

The names express composition; but, as this is binary, each denomination is formed of two words. The class of oxygenated compounds served as a model for all the others.

The simplest compounds of oxygen are acids and oxides. These two words both indicate the presence of oxygen; they mark the genus of the combination; the species is indicated by another word, generally an adjective, which recalls the name of the simple body, metalloïd or metal, combined with the oxygen. Thus we say sulphuric acid, and lead oxide, oxide of lead, or plumbic oxide.

Do we desire to express the several degrees of oxidation of one and the same body? The nomenclature is fertile in ingenious artifices: it places

Greek prefixes at the head of one or the other of the words above mentioned, or it adds an adjective of variable termination. Thus it marks the several degrees of oxidation of sulphur by the names, hyposulphurous, sulphurous, and sulphuric acid. The degrees of oxidation of lead and manganese are indicated by the following denominations: protoxide of lead, dioxide of lead; protoxide of manganese; peroxide of manganese.

Two words are used in like manner to designate salts, the one marking the genus, determined by the acid, and the other the species, determined by the metallic base. Thus lead sulphate, sulphate of lead, or plumbic sulphate, signifies a compound of sulphuric acid and lead oxide; sulphite of potash, potash sulphite, or potassic sulphite, a compound of sulphurous acid and potash.

The same principles were applied to the compounds formed by sulphur and phosphorus with metals.

This, however, is not the place to insist upon details, our object being merely to illustrate the influence of the new names on the extension of the new ideas. From the year 1790, the fundamental idea of Lavoisier's system, that is to say, the dualism of compounds, was insinuated into the mind of the reader, whether philosopher or student, together with the very names of the language of chemistry; and we know how great, in such cases, is the power of words.

This system, though based upon facts, was not free from hypotheses. Regarding salts as containing two distinct elements, and assuming in them the partition of the oxygen between the acid and the base, it pre-supposed a certain grouping of the elements, which was not capable of direct demonstration. It was, in reality, a hypothesis. Clearly indicated in the language, it has been impressed upon the minds of chemists, and transmitted, as a demonstrated truth, from generation to generation. It possessed, in fact, both simplicity and probability. Not only did it account for all known facts, but it further led to the discovery of new facts of the greatest importance: it was good because it was fertile.

It was known at the end of the last century that the alkalis, alkaline earths, and earths, such as potash, lime, and alumina, possess the property of uniting with acids to form salts, and, nevertheless, these salifiable bases had not been decomposed. In comparing them with oxides, Lavoisier divined their nature, but no one had yet separated from them the metallic radicals. Since 1790, numerous experiments, undertaken with the object of reducing the alkalis and earths, had ended only in failure; and, by these numerous disappointments, chemists had been discouraged to such a degree, that the great discovery of Sir Humphry Davy was received in 1807 with real surprise.

But the fact announced by the great English chemist, of the reduction of the alkalis by the current of a powerful battery, was soon confirmed by the very men who had at first received it with doubt, namely, Gay-Lussac and Thénard. We know that these chemists succeeded in reducing potash and soda by submitting them to the action of iron at a very high temperature. Certain earths, however, such as alumina and magnesia, resisted these powerful means of reduction. But after Oersted had shown the means of converting these earths into anhydrous chlorides, by the simultaneous action of chlorine and carbon at a red heat, Wöhler first conceived the idea of decomposing these anhydrous chlorides by means of the alkali-metals discovered by Davy, and had the glory of realising it. He thus isolated aluminium, which, in the hands of H. St. Claire Deville, has since become an ordinary metal.

All these discoveries, which have shed lustre on the greatest names of chemistry in this century, flow from one idea—that, namely, of the constitution of salts, proposed by Lavoisier.

On another point, the theory had been found defective. Lavoisier at first supposed that all acids contained a common element, which he called oxygen, because he regarded it as the acidifying principle or generator of acids. This proposition, though exact in many cases, was too absolute in its enunciation.

Berthollet, in 1789, demonstrated its exaggeration by the analysis of sulphuretted hydrogen and prussic acid, both of which bodies are free from oxygen, and yet possess acid properties. But one of the most important exceptions to Lavoisier's rule is exhibited by muriatic acid, the composition of which was discovered at a later date.* It is an energetic mineral acid. It neutralises potash like sulphuric acid, giving rise to analogous phenomena, a notable rise of temperature, and the formation of a white, neutral, saline substance, which, if the liquids are concentrated, is precipitated in small crystals. In both cases, an acid is neutralised by a base, with formation of a salt, and yet the first of these acids does not contain oxygen.

As it frequently happens in science, these facts, embarrassing at first for the theory, and regarded as exceptional, have become the starting-point of a new generalisation.

Davy made them the ground-work of a theory of salts, which was supported by Dulong, but rejected by their contemporaries as contrary to established ideas. At the present day, however, it is admitted, and we shall have to explain it hereafter. One more remark, to complete this part of our subject. This great step, which consists in including within the same order of phenomena, and explaining by the

* Note 1, at the end.

same theory, the neutralisation of bases by hydracids and oxacids, and has overthrown the theory of Lavoisier on the constitution of acids, is based on facts discovered by Berthollet at the very time when this theory had just won its first triumphs. It carried, therefore, almost in its birth, the germ of its destruction.

DALTON AND GAY-LUSSAC.

I.

At the time when Lavoisier laid the foundation of the new chemistry, a German philosopher, Wenzel, was working obscurely to enlarge and define, by exact analyses, the notions then existing on the composition of salts. The chemists of that time had been struck by the fact that two neutral salts can form, by exchange of bases and acids, two new salts, neutral like the first. Thus, on mixing concentrated and neutral solutions of sulphate of potash and nitrate of lime, there are formed, by double decomposition, sulphate of lime, which is precipitated, and nitrate of potash, which remains in solution. The two new salts are neutral like the two others, and the permanence of the neutrality was the point to be explained. Wenzel was so fortunate as to discover the explanation. He showed that when two neutral salts are mixed in such quantities that the acid of the first is exactly neutralised by the base of the second, it likewise happens that the acid of the second is exactly sufficient to

neutralise the base of the first. In other words, he showed that when two neutral salts decompose one another reciprocally, the neutrality is preserved, because the relative quantities of any two bases which neutralise a given weight of a certain acid, are exactly those which neutralise a determinate weight of any other acid.

Hence follows the law of equivalents, which was developed twenty years later by Richter. The quantities of different bases which neutralise 1000 grammes of sulphuric acid, are proportional to the quantities of the same bases which neutralise 1000 grammes of nitric acid. The former are equivalent among themselves; that is to say, they can replace one another with regard to a certain weight of sulphuric acid. It is the same with the second quantities, which can replace one another with regard to a certain weight of nitric acid. If the weight of the acid does not change, the weight of each of the bases remains constant; if the weight of the acid increases or diminishes, the weight of each of the bases increases or diminishes in the same proportion.

The proportions by weight in which acids combine with oxides are therefore absolutely fixed: such is the fundamental fact, deduced from the researches which were undertaken at the end of the last century on the composition of salts. The law of equivalents implies the law of definite proportions.

The theoretical consequences which are deduced from the labours of Wenzel, and give them so high a degree of importance, were scarcely noticed, and the discoveries of the Freiberg chemist, completed by those of Richter,* soon fell into profound oblivion. The hour of Wenzel and of Richter was not yet come. Their contemporaries were engaged in discussing theoretic ideas of a higher order. The contests and triumphs of Lavoisier then captivated the minds of all; and, nevertheless, the facts in question, interpreted as they were destined to be twenty years later, would have furnished a confirmation and support of the new system.

But the theoretical interpretation was still wanting. It flows from the labours of an English philosopher, who has enriched the science with a conception, at once the most profound and the most fertile of all those which have arisen since the time of Lavoisier.

II.

At the beginning of this century, chemistry was taught at Manchester by a man who joined to an ardent love of science that noble pride of the philo-

* Richter published some inexact analyses, and had the ill fortune to adapt them to theories still more erroneous. This circumstance discredited all his labours, the merit of which was not recognised till twenty years later by Berzelius.

sopher which knows how to prefer independence to honours, and the glory of solid labours to a vain popularity. This professor was Dalton; his name is one of the greatest in chemistry.

Having studied the composition of two gases formed of hydrogen and carbon—namely, marsh-gas and olefiant gas—he perceived that the latter contains, for the same quantity of carbon, exactly half as much hydrogen as the former. He made similar remarks respecting the composition of carbonic acid and carbonic oxide, and that of the oxygenated compounds of nitrogen. These researches led to general laws, which may be thus enunciated: When a body forms with another several combinations, if the weight of one of these bodies be regarded as constant, the weight of the other varies according to very simple numerical proportions: 1 to 2, 1 to 3, 2 to 3, 1 to 4, 1 to 5, &c. Such is the law of *multiple proportions*, formulated by Dalton.

So great a discovery happily completed those of Wenzel and Richter. Those chemists had shown that combination between bases and acids takes place in fixed and definite proportions. Dalton found that the same law holds good in combinations formed between simple bodies. To the fact of definite proportions he added that of multiple proportions. The importance of these labours would not, perhaps, have been fully recognised, had not the author's elevated

and deep-thinking mind succeeded in interpreting the facts which he had discovered, by a striking hypothesis, and expressing them by a formula of great simplicity. Reviving the idea of Leucippus and the expression of Epicurus, he supposed that bodies are formed of small individual particles, which he called *atoms*. To this old and vague notion he attached an exact meaning, by supposing, on the one hand, that the atoms of each kind of matter possess a constant weight, and, on the other, that combination between two kinds of matter takes place, not by penetration of their substance, but by juxtaposition of their atoms.

This fundamental hypothesis being admitted, the fact of definite proportions and the fact of multiple proportions are simply and satisfactorily explained.

The definite proportions in which bodies combine represent the constant ratios between the weights of the juxtaposed atoms.

Multiple proportions indicate the variable numbers of atoms of the same kind, which may unite with one or several atoms of another kind, this latter case being that in which several compounds are formed by the union of the same two bodies.

Now, as these multiple combinations can be produced only by the addition of new entire atoms, it follows evidently that the numerical ratios between these atoms must be integral, and for the most part simple. Moreover, the ratio between the atoms of

one element and those of another, remains constant in any one of the compounds which they form, whatever may be the weight taken into account. If, then, in compounds formed by the union of two elements in various proportions, we take quantities containing a constant weight of one of these elements, it is clear that the variable weights of the second must be multiples one of the other, just as the atoms of the one element are with regard to those of the other in the ultimate molecules.

The definite and multiple proportions according to which bodies combine, represent the weights of their atoms—not the absolute, but the relative weights. They are numbers expressing relations of weight. The term of comparison is the weight of one of the atoms taken as unity. Dalton chose hydrogen for the unit. If the atom of hydrogen weighs 1, what will be the weight of an atom of oxygen? It will be 7, according to Dalton, who supposed that 7 parts of oxygen are required to form water with 1 part of hydrogen. We now know that the number 7 is inexact, and that water is formed of 8 parts of oxygen combined with 1 part of hydrogen. But the point to be established is, that the numbers 1 and 7, which Dalton regarded as the atomic weights of hydrogen and oxygen, represented precisely the proportions according to which these bodies were then supposed to combine to form water. His opponents could not

deny this fact, but, rejecting the theoretical interpretation, they refused also to accept the word. These atomic weights of Dalton were called *equivalents* by Wollaston, *proportional numbers* by Davy; and we see that these notions of atomic weights and equivalents, which have since been separated, were originally confounded together, and represented nothing but the proportions by weight in which bodies combine. It must also be observed that the numerical determinations published by Dalton were far from being exact—a circumstance which may have given rise to criticism, but by no means impairs the grandeur of his discovery or the force of his conception.

The following is an important point, deduced by Dalton himself, from the notion of atoms. If a given compound be formed by the juxtaposition of atoms of different nature, each having a definite weight, it is clear that the sum of the weights of these atoms must represent the weight of the compound; and the smallest conceivable quantity of this compound will be that which contains the smallest possible number of elementary atoms. This is what is called a *molecule* of a compound body, and the weight of this molecule will evidently be formed of the sum of the weights of all the elementary atoms which it contains. But compound bodies, in combining together, follow the same laws as simple bodies. They attract one another, and place themselves together by entire molecules;

that is to say, all the atoms forming the molecule of one of the compound bodies are carried as a whole towards all the atoms which constitute one or several molecules of another compound body. Thus, when carbonic acid unites with lime, all the elementary atoms which constitute the molecule of the acid are added to the atoms which constitute the molecule of lime, and thus there is formed a molecule of carbonate of lime. It follows that such combinations must take place, like those above mentioned, in definite and multiple proportions:

In definite proportions, because it is impossible to conceive less than one molecule uniting with another molecule, the two possessing, moreover, a determinate weight.

In multiple proportions, because, when one compound body is capable of forming several combinations with another compound body, 1 or 2 molecules of the one must attract 1, 2, 3, &c. entire molecules of the other.

We see, then, that the law of definite proportions, thus enlarged and interpreted by Dalton, included, as a particular case, the laws of the composition of salts, discovered by Wenzel and Richter. Thus we may say that the work of the great English chemist may be summed up in these three points:—

The law of definite proportions confirmed and generalised.

The law of multiple proportions introduced into the science.

These two laws connected together and theoretically interpreted by the hypothesis of atoms.

Dalton found in his fellow countryman Thomson a convinced interpreter, but opponents were not wanting. The celebrated 'System of Chemistry,' in which Thomson, in 1807, made known the discoveries and ideas of Dalton, having been translated into French, Berthollet placed at the head of this translation a preface, written in 1808. In this preface he makes a violent attack on the atomic theory, and even on the fact of definite proportions. Both the one and the other were little in accordance with the opinions which he had himself put forth on the relations by weight of elements in compounds.

The profound researches of Berthollet on affinity are well known. All bodies possess affinity one for the other in different degrees, but this chemical force is subject to the influence of various physical forces, such as elasticity and cohesion, which may modify it deeply. When two salts are mixed together, the two acids have a tendency to divide the two bases between them, and two new salts have a tendency to form by virtue of a double decomposition, that is to say, of an exchange of bases and acids. Nevertheless, this exchange is incomplete, and the decomposition stops at a certain point, so that the two new salts remain

mixed with a certain portion of the original salts which remain undecomposed. But if one of the new salts is insoluble or volatile, the decomposition takes place completely: for this salt is removed out of the way by its elasticity if it volatilises, by its cohesion if it is precipitated, and its elements can exert no further action within the mixture.' It is thus that affinity, the cause of chemical reactions, is influenced, according to Berthollet, by the intervention of certain physical forces, these latter forces sometimes alone determining the formation of compounds in definite proportions. In this manner:—

Two bodies are in contact; the cohesion of the one is not overcome by affinity until a certain proportion of the other body is brought to bear upon the first. The elements of the two bodies then unite according to a fixed proportion by weight. Or, again, two bodies are capable of uniting in various proportions, but among the possible combinations one is distinguished by predominance of cohesion or of elasticity. The elements of this latter body are then combined in definite proportions, because it crystallises, or because it is insoluble or volatile.

Berthollet, then, admits definite proportions, not as a general law, but as an accidental result produced under the influence of forces foreign to affinity. When these latter forces, cohesion and elasticity, balance one another, either in the component bodies

or in the products of their combination, affinity, freed from these obstacles, can exert itself without restraint, and is subject only to the influence of masses. Combination, and chemical action in general, may then take place in any proportions whatever, according to the masses which act upon one another. We may easily understand what kind of reception the celebrated author of these propositions was likely to give to the ideas of Dalton: he attacked them vigorously. But his great authority could not prevail against the authority of facts. The contrary view was sustained by Proust, who combated the arguments of his adversary by exact analyses of oxides and sulphides. This discussion, commenced in 1801, was continued till 1808. The remembrance of it is imperishable, both on account of the greatness of the results obtained, and of the rare qualities displayed by the champions, both of them powerful in the strife and equally animated by respect for truth and courtesy.

The law of definite proportions, a fundamental law of chemistry, issued triumphant from this great debate. Since then it has been universally received; and why should we not say that it has received a striking confirmation in our own days? This truth, revealed by approximate analyses to the genius of Wenzel, Richter, Proust, Dalton, and Wollaston, has recently been established by Stas, by determinations so exact that they come very near to absolute precision.

According to Wenzel, Richter, and Proust, we may admit a great law of nature; according to Stas, we may assert that this law is not subject to sensible perturbations.

III.

In the first years of the present century, when the question under consideration was being debated by the masters of the science, a young philosopher, who had scarcely completed his course at the École Polytechnique, was preparing himself by earnest study and exact work for the most brilliant discoveries. Joseph-Louis Gay-Lussac, 'élève ingénieur' in 1808, was himself about to become a great master. His researches on the volumetric proportions in which gases combine together, have led to the double result of furnishing a new and decisive argument in favour of the law of definite proportions, and of giving to the atomic theory a firm support and a new expression.

Let us first recapitulate the facts.

The proportions by volume according to which hydrogen and oxygen gases combine to form water were not fixed with certainty. It had been supposed at various times that this combination takes place in the proportion of 12 volumes of oxygen to 23 volumes hydrogen, of 100 volumes oxygen to 205 volumes hydrogen, of 72 volumes oxygen to 143 volumes hydrogen. Gay-Lussac, in 1805, in conjunction with

A. von Humboldt, showed that the two gases unite *exactly* in the ratio of 1 volume of the former to 2 volumes of the latter.

Generalising this observation, he showed in 1809 that there exists a simple ratio, not only between the volumes of two gases which combine, but also between the sum of the volumes of the combining gases and the volume occupied by the compound itself, measured in the gaseous state.

Thus 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of vapour of water. Two volumes of nitrogen are combined with 1 volume of oxygen in 2 volumes of nitrogen protoxide.

In these two cases, 3 volumes of the component gases are reduced by combination to 2 volumes: the ratio of 3 to 2 is simple. In other cases we observe the ratio of 2 to 2, or of 4 to 2. Thus, 1 volume of chlorine unites with 1 volume of hydrogen to form 2 volumes of hydrochloric acid, 3 volumes of hydrogen unite with 1 volume of nitrogen to form 2 volumes of ammonia.

The influence of Gay-Lussac's discovery is immense. To understand the consequences which flow from it, let us compare it with the facts previously discovered.

Bodies combine in definite proportions by weight, which express, according to Dalton, the relative weights of their atoms.

Gases combine in simple and definite proportions

by volume; that is to say, a simple ratio may be observed between the volumes of the gases which enter into combination.

If, then, we apply to gases the hypothesis of Dalton, is it not evident that the weights of the volumes of gases which combine must represent the weight of their atoms? Let us take an example. If 1 volume of chlorine unites with 1 volume of hydrogen, the weight of 1 volume of chlorine must represent the weight of 1 atom of chlorine, and the weight of 1 volume of hydrogen must represent the weight of 1 atom of hydrogen. But the weights of equal volumes of gases, referred to one amongst them, are what are called their densities. There must then exist a simple relation between the densities of gases and their atomic weights.

This relation exists. We shall see that the densities of gases are proportional to the weights of their atoms, or to simple multiples of these atomic weights.

We see, then, that the discovery of Gay-Lussac, after having afforded a powerful confirmation of the law of definite proportions, has also lent an efficient support to the atomic theory, by showing that the densities of gases afford a means for the determination or the verification of atomic weights. And yet, by a remarkable coincidence, these two corollaries of the discovery in question were misunderstood, even by those who had the greatest interest in bringing

them to light and promoting their acceptance. Dalton doubted the exactness of the facts advanced by Gay-Lussac. Gay-Lussac, for his own part, was of opinion that the fact of simple and definite proportions between the volumes of gases which combine might be reconciled with the opinion of Berthollet, that bodies in general unite in very variable proportions.* Thus he endeavoured to save the ideas of Berthollet at the very moment when he was dealing them a decisive blow.

We have just noticed the existence of a simple relation between the densities of gases and the weights of their smallest particles. Shortly before the date of Gay-Lussac's discovery, an Italian chemist had endeavoured to define this relation. In a memoir published in 1811, Amedeo Avogadro† enunciated the opinion that gases are formed of material particles sufficiently removed from one another to be free from all reciprocal attraction, and subject only to the repulsive action of heat. These little masses he called integrant or constituent molecules. In assuming the gaseous form, matter is resolved, according to his ideas, into integrant molecules, the numbers of which are equal for equal volumes. Hence it follows

* Mémoires de la Société d'Arcueil, t. i. p. 232.

† Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans les combinaisons. Par A. Avogadro, *Journal de Physique*, t. lxxiii. p. 58. Juillet 1811.

that in gases, the weights of these integrant molecules are proportional to the densities.

Avogadro applied this proposition to all gases, simple or compound. According to his view, therefore, the integrant molecules were not atoms properly so called, that is to say, little masses indivisible by chemical forces, but groups of atoms united together by affinity, and set in motion by heat. In a word, they constituted what are now called molecules. These molecules being present in equal numbers in equal volumes of different gases, it is evident that heat ought to separate them equally. Consequently the hypothesis of Avogadro, as indeed he himself remarks, explains the fact that the same variations of temperature and pressure produce in all gases nearly the same changes of volume.

This conception, simple and exact as it is, appears to have escaped the notice of his contemporaries, either because the author did not possess the authority necessary to ensure its adoption, or because he brought it into discredit by endeavouring to extend his hypothesis to non-gaseous bodies. This hypothesis was reproduced by Ampère in 1814.* He designates Avogadro's integrant molecules as par-

* Lettre de M. Ampère à M. le comte Berthollet sur la détermination des proportions dans lesquelles les corps se combinent, d'après le nombre et la disposition relative des molécules dont leurs particules intégrantes sont composées (*Annales de Chimie*, 1re série, t. xc. p. 43; 30 avril 1814).

ticles, and the atoms as molecules. 'I started,' says he, 'from the supposition, that when bodies pass to the state of gas, their particles alone are separated by the expansive force of caloric, to distances much larger than those at which the forces of affinity and cohesion exert an appreciable action, so that these distances depend only upon the temperature and pressure to which the gas is subjected, and that, at equal temperatures and pressures, the particles of all gases, whether simple or compound, are placed at the same distance from one another. On this supposition the number of the particles is proportional to the volume of the gas.'

Those particles which are moved by heat are supposed by Ampère to be formed of a more or less considerable number of molecules, that is to say, of atoms. Thus Ampère was careful not to confound particles with the atoms which compose them.

This confusion has, however, arisen at a later date, for the word atom has often been used in the sense which Ampère attached to the word particle. Berzelius, the great promoter of the atomic theory, admitted the existence of several kinds of atoms—simple atoms and compound atoms. This last expression, which was faulty, denoted Ampère's particles. Thirty years ago, it was said that 'equal volumes of gases, under the same conditions of pressure and temperature, contain equal numbers of

atoms.' In the sense which we now attach to the word atom, this proposition is true only for a certain number of simple gases: oxygen, hydrogen, chlorine, nitrogen, &c. It is inexact if applied to *all* simple substances and to compounds, considered in the state of gas or vapour. We now know, thanks to the researches of Dumas, that the vapours of phosphorus, arsenic, and mercury, do not contain in equal volumes the same number of atoms as hydrogen, oxygen, nitrogen, &c. A similar remark applies to compound gases. Thus, ammonia gas contains 1 atom of nitrogen and 3 atoms of hydrogen, that is to say, 4 atoms; whereas hydrochloric acid gas contains, in the same volume, only 1 atom of hydrogen and 1 atom of chlorine, or, altogether, 2 atoms. Nevertheless, compound gases are subject to the same laws of expansion as simple gases. Ampère and Avogadro had regard to the one class as well as to the other. They supposed all gases to be formed, in equal volumes, of the same number of particles placed at equal distances, and obedient, in the same manner, to the action of heat. Their idea was just. It follows from the discoveries of Gay-Lussac; adapts itself to the hypothesis of Dalton; affords an explanation of the physical properties of gases; and yet it has never obtained the unanimous assent of chemists. As applied to atoms, and enunciated in the terms above given, it was a striking but inexact formula; and it

is only in our own time that it has attained a correct expression and consistent development. Hence it happened that the beautiful conception of Avogadro and Ampère remained for forty years almost barren as regards the atomic theory. The latter has, nevertheless, taken its upward flight; but the impulse has come from another side.

BERZELIUS.

Berzelius, the great successor of Lavoisier, completed his theory of dualistic chemistry. He gave to the atomic theory, on the one hand, a solid foundation by his determinations of atomic weights, as exact as they are numerous, and on the other, a new expression by the use of formulæ adapted to the idea of dualism. Moreover, he attempted to explain dualism itself by the electro-chemical hypothesis. Such, in few words, is the great part due to Berzelius in the progress of ideas.

I.

Jacob Berzelius was born in 1779, at Wafnersunda, in West Gothland. He died at Stockholm, in 1848. In the course of a long career entirely devoted to science, he acquired the most undisputed authority, and exhausted all the honours which can fall to the lot of a man of science: noble and academic titles, a high position in Education and in the State, fortune and public recognition— all these rewards united to

crown, but not to diminish in him, the taste and the worship of science. He worked to his latest day. Author of numerous and important discoveries, he owed more to perseverance than to genius. That which excites admiration in his labours is the exactness of the facts observed, and the consequent rigour of his deductions, rather than the brilliancy and the depth of his ideas. He raised the methods of analysis to a degree of perfection unknown before, thus himself producing the instrument of his great discoveries.

He first discovered the oxides of cerium,* also selenium (1818), and thorina (1828); he isolated silicium, zirconium, and tantalum. Such discoveries command attention by their importance, but they have been less fruitful in connection with the progress of theory than the researches pursued by Berzelius during thirty years, on the determination of atomic weights.

Dalton published, in 1808, in his 'New System of Chemical Philosophy,' a table of atomic weights. He chose for unity the weight of the atom of hydrogen. The numbers which he gave for the atomic weights of seventeen other simple bodies, though exact enough in some cases, differ considerably from the true values for the greater number of the elements. These differences are less considerable in the

* In conjunction with Hisinger, in 1803.

table given by Wollaston in 1813,* in which the atomic weights, or rather the equivalents (this word was introduced by Wollaston) are referred to the equivalent of oxygen, which he made equal to 10. The tables published by Berzelius are more complete and likewise more exact. In them he referred the atomic weights to that of oxygen supposed equal to 100. The quantity of a metal capable of forming with 100 parts of oxygen, the first degree of oxidation, was generally taken for the atomic weight of that metal. In some cases he departed from this rule, as for example, for certain non-metallic bodies, and likewise for various metals. Wollaston, adopting the idea of Dalton, had assumed for the atomic weight of hydrogen, the quantity by weight of hydrogen capable of uniting with 10 parts, that is to say, 1 atom, of oxygen. In other words, the atomic weights of hydrogen and oxygen represented the relative proportions in which the two bodies unite to form water, this compound resulting from the union of 1 atom or equivalent of hydrogen with 1 atom or equivalent of oxygen. We see, then, that the terms atom and equivalent were here used synonymously. Berzelius, on the contrary, relying on the discoveries of Gay-Lussac, supposed that water, which results from the union of 2 volumes of

* *Annales de Chimie*, t. xc. p. 138.

hydrogen and 1 volume of oxygen, is composed of 2 atoms of hydrogen and 1 atom of oxygen. He accordingly took for the atomic weight of hydrogen, the weight of 1 volume of this gas, that of 1 volume of oxygen being represented by 100.

It is thus that the distinction between atoms and equivalents was first introduced into chemical science: it follows from the discoveries of Gay-Lussac, as interpreted by Avogadro and Ampère. It appears for the first time in the tables of Berzelius. In Dalton's system the atoms represent the proportions in which bodies combine, and the atomic weights are the same as the equivalents. In that of Berzelius the atoms represent gaseous volumes, and the atomic weights are nothing else than the relative weights of equal volumes of the gases. For a certain number of gaseous bodies, an equivalent is formed of 2 atoms. Such is the case, not only for hydrogen, but also for nitrogen, chlorine, bromine and iodine, these latter being supposed to be reduced to vapour. The atomic weights of these bodies represent the weights of 1 volume; but since it requires 2 volumes of nitrogen, chlorine, &c. to form with 1 volume of oxygen the first degree of oxidation, it is clear that the weights of 2 volumes of nitrogen, chlorine, &c. represent equivalents of these bodies with respect to oxygen. Berzelius supposed that the atoms of hydrogen, nitrogen, chlorine, bromine and iodine are

united two by two. He called these couples 'double atoms,' and supposed them to be indissolubly united, so as to represent precisely the equivalents of these gases; that is to say, the smallest proportions capable of entering into combination. Thus water, according to his views, contained 1 atom of oxygen united with a double atom of hydrogen; hydrochloric acid contained a double atom of hydrogen united with a double atom of chlorine; ammonia was formed of a double atom of nitrogen united with three double atoms of hydrogen. In a word, no compound of hydrogen, chlorine or nitrogen contained less than two atoms of these elements, these two atoms being the smallest proportions capable of existing in a compound. This smallest proportion represents an equivalent. Thus the idea of double atoms offered the means of reconciling former ideas with the discoveries of Gay-Lussac. The atomic weights of the gaseous elements represented the relative weights of their volumes, and for some of these simple gases two atoms formed that which Dalton had regarded as a single atom, and Wollaston had named an equivalent.

If the principles which guided Berzelius in the determination of his atomic weights marked a sure progress, it must be allowed, on the other hand, that the idea of double atoms led him to inexact conceptions respecting molecular magnitudes. A molecule of water certainly results from the union of 2 atoms

of hydrogen with 1 atom of oxygen; but when 2 atoms of hydrogen unite with 2 atoms of chlorine, do they form, as Berzelius supposed, a single molecule of hydrochloric acid? By no means. Such a molecule would have twice the normal magnitude. We know at the present day that the molecule of hydrochloric acid contains only 1 atom of chlorine and 1 atom of hydrogen, and that the molecule of ammonia contains only 1 atom of nitrogen combined with 3 atoms of hydrogen. These molecules, in the state of gas, occupy the same volume as a molecule of water-vapour. Such is the conception which flows from the development consequent on the theory of volumes. Berzelius, who was one of the first to travel on this new road, did not reach the end of it. That honour was reserved for Gerhardt.

But the great Swedish chemist has rendered to theory a service of another kind. He is the author of a notation adapted to indicate the atomic composition of bodies.

The alchemists, with the view of abbreviating or obscuring their language, were accustomed to substitute for names, certain symbols, of fantastic shape. These symbols were purely conventional, and represented nothing but words. To Dalton is due a more rational attempt. The symbols which he proposed represented atoms. They were little circles enclosing marks characteristic of the

several elementary bodies; those of hydrogen had a point in the centre, those of nitrogen a bar, those of sulphur a cross, while those of oxygen did not enclose anything. The atoms of carbon were black, as was appropriate. Those of the metals had in the middle the initial letter of the name of the metal. To represent compound bodies, Dalton grouped together the atoms of their elements. Water being formed, according to his view, of 1 atom of oxygen and 1 atom of hydrogen, was represented by the symbols of these two atoms placed side by side. Sulphuric acid formed a group of 4 circular atoms, 3 atoms of oxygen being disposed symmetrically round 1 atom of sulphur placed in the middle. Acetic acid contained 6 atoms, 2 black atoms of carbon forming, as it were, the axis of the molecule, and each being flanked by 1 atom of oxygen and 1 atom of hydrogen.

All this was very ingenious and very clear. To acquire a knowledge of the atomic composition of a body, it was in fact sufficient to count the number of these atoms, which were spread out, in a manner, side by side. The only inconvenience of this graphic representation of molecules was the space which it took up on the paper, as soon as the composition of bodies became a little complicated. And further, was there not something arbitrary in the symmetrical arrangement which Dalton endeavoured to

give them? Berzelius knew how to avoid these rocks; he conceived the idea of representing atoms by the initial letters of the Latin names of all the elements: O signified an atom of oxygen, H an atom of hydrogen, K an atom of kalium or potassium, Sb an atom of stibium or antimony. A compound formed of two different atoms was represented by two letters placed side by side; if it contained several atoms of one and the same element, the symbol of that element had attached to it a coefficient indicating the number.

Thus, sulphuric acid was represented by the formula SO^3, ammonia by the formula N^2H^6. This system of notation, so simple in its principle, adapted itself in application to all hypotheses respecting the grouping of atoms, and to the interpretation of the most complex reactions.

The dualistic theory was then predominant, and Berzelius introduced it into his formulæ. The starting-point was the theory of salts. Richter had observed that the quantities of different bases which neutralise the same weight of acid contain equal quantities of oxygen, and that, consequently, there exists in the same class of salts a constant ratio between the quantity of oxygen in the base and the quantity of acid. To this exact proposition Berzelius added a feature which rendered it complete; he remarked that for each class of salts there exists a

constant and simple ratio between the oxygen of the base and that of the acid. In the sulphates the acid contains three times as much oxygen, in the carbonates twice, in the nitrates five times as much oxygen as the base. These laws of the composition of salts are expressed in the notation in the clearest manner. The different proportions of oxygen represent atoms in different numbers. If, then, we represent the composition of a salt by the formula of the acid placed next to that of the oxide, it is clear that the ratio between the quantities of oxygen in these two elements will be necessarily expressed by the numbers of oxygen atoms contained in each of them. For 3 atoms of oxygen contained in the acid of the sulphates, these salts must contain 1 atom of oxygen in the oxide: hence the law of composition of salts discovered by Berzelius is rendered evident by the mere inspection of their formulæ.

By the very arrangement of these formulæ in which the acid appeared on one side with the train of oxygen-atoms belonging to it, and the metallic base on the other with the oxygen united to the metal, Berzelius gave to the dualistic system a degree of precision unknown before his time. He likewise added an important development, in proving that, just as acids can unite with oxides, so likewise can chlorides and sulphides unite among themselves. Thus, chloride of platinum unites with chloride of

potassium. The double chloride thus formed is a kind of salt, a chloro-salt; chloride of platinum plays in it the part of acid, the chloride of potassium that of base. There likewise exist sulphides capable of playing the part of acids, others which act as bases, and the sulphides of these two classes unite together to form sulphur salts. In the notation the composition of these non-oxygenated salts was expressed by two juxtaposed formulæ, the first representing the acid element, the second the basic element. Thus, the system grew, not only by the striking expression given to it by the atomic formulæ, but likewise by important additions.

II.

A SCIENTIFIC system is not really worthy of the name unless it embraces every order of important facts. Dualism was especially applicable to mineral compounds; it was not easy to include within it the notions already acquired of the constitution of organic compounds. It was known that the proximate principles which nature has diffused through the organism of plants and animals, contain three or four elements, carbon, hydrogen, oxygen, to which is often added nitrogen. Among so great a number of different substances, bodies had been observed which played the part of acids, others which were neutral; and lastly, there had recently been discovered sub-

stances possessed of basic properties, that is to say, capable of uniting with acids to form definite salts. With regard to the organic acids, Berzelius adopted the ideas previously suggested by Lavoisier. Vegetable acids contain a radical united with oxygen, and this radical is formed of carbon and hydrogen combined in such a manner as to form only a single 'base.' Vegetable acids differ from one another in the proportions according to which the elements are united in the radical, and by their degree of oxygenation. As to the acids obtained from the animal kingdom, their composition is more complex: they contain radicals in which the hydrogen and carbon are often associated with nitrogen, sometimes with phosphorus. Such were the views of Lavoisier.*

The atomic theory and the progress of analysis enabled Berzelius to develop these views and make them more precise; he first fixed the 'equivalents' of the principal organic acids, that is to say, the relative magnitudes of their molecules, by determining the relative quantities of those acids which unite with one equivalent of lead oxide or silver oxide. Organic analysis, the principle of which had been indicated by Gay-Lussac and Thénard, and the processes of which had just been improved by Chevreul, taught him the proportions of the elements in the several

* *Traité de Chimie*, t. i. p. 497.

acids, and consequently the number of elementary atoms in their 'equivalents' or molecules.

Grouping together the atoms of carbon and hydrogen, or of carbon, hydrogen and nitrogen, he formed of them the binary or ternary radicals which enter into the composition of acids, or in general of oxygenated compounds of organic origin. According to him, the radical of formic acid, which he calls formyl, is constituted of 2 atoms of carbon and 3 atoms of hydrogen; that of acetic acid, which he calls acetyl, contains 4 atoms of carbon and 6 atoms of hydrogen. But formyl and acetyl combine with 3 atoms of oxygen to produce formic and acetic acids respectively. We here recognise the ideas of Lavoisier, taking the simple and precise form given to them by the advance already made. Berzelius extended these views to all oxygenated compounds. 'Organic substances,' said he, 'are formed of oxides containing compound radicals.'*

Amongst these oxides there is one which has given rise to important researches and animated discussions. This oxide is ether, the product of the action of sulphuric acid on alcohol. It has been known for ages, and has given its name to a numerous class of compounds designated as ethers. The relations of

* *Traité de Chimie*, édit. française, 1830, t. ii. p. 111. The idea of organic radicals was developed by Berzelius subsequently to 1817, in the second Swedish edition of his Treatise.

this body to alcohol had been fixed since 1816 by Gay-Lussac, who expressed them as follows: the two substances contain 2 volumes of olefiant gas combined, in alcohol with 2 volumes, in ether with 1 volume of vapour of water.

MM. Dumas and Boulhay have published a memoir upon the ethers called compound, which marks an epoch in the science. They observed that these bodies contain the elements of an acid combined with exactly 2 volumes of olefiant gas and 1 volume water-vapour; that is to say, with the elements of ether. Assigning to olefiant gas a function analogous, up to a certain point, to that of ammonia, they compared the ethers with ammoniacal salts. This was the first time that in organic chemistry a series of analogous phenomena had been grouped together by theory, and that the facts relating to the formation, composition, and transformation of an entire class of bodies received a simple interpretation by means of atomic formulæ and equations.

To this theory of the ethers Berzelius some years later opposed another. Comparing them with salts properly so called, he assumed in them the existence of an organic oxide, which was no other than ether. This oxide contained, according to him, a radical formed of 4 atoms of carbon and 10 atoms of hydrogen. In ether, this radical, designated by Liebig as *ethyl*, is combined with 1 atom of oxygen. But

this ethyl can also unite with chlorine and with other simple bodies, thus forming a chloride or other binary combination. Chloride of ethyl is nothing else than the hydrochloric ether discovered long ago. Common ether, which is the oxide of ethyl, can combine, like metallic oxides, with water to form a hydrate, which is alcohol, and with anhydrous acids to form true salts, which are the compound ethers. All these compounds are binary.* Such are the principal features of this beautiful conception, which marks the most brilliant phase of the theory of organic radicals.

This theory has been the object of prolonged discussion. It assumes, said its opponents, the existence of numerous hypothetical bodies; for, after all, this ethyl, and the other numerous radicals, are merely imaginary bodies having no real existence. They will be discovered, replied its partisans. Has not Gay-Lussac isolated cyanogen? has he not shown that this compound body, formed of carbon and nitrogen, reacts like a simple substance? Do we not know, on the other hand, that sulphurous acid unites directly with oxygen, and carbonic oxide with chlorine and with oxygen?

These arguments were weighty. The discovery of cacodyl by Bunsen, at a later date, gave them powerful support. What more conclusive example could be

* Note 3, at the end.

found to oppose to the adversaries of the radical theory, than this body, formed of carbon, hydrogen, and arsenious acid, possessing so extraordinary a power of combination, capable of uniting directly and in several proportions with oxygen, sulphur, and chlorine, and so energetic in its affinities that it burns spontaneously in the air, and takes fire in chlorine like arsenic itself? And was it not a flat denial of evidence to refuse the character of a radical to cyanogen and to cacodyl, and not to admit in these compound bodies a force analogous to that which impels one elementary body towards another? The attempt was made, however, by regarding the phenomena exclusively from the point of view of another celebrated theory, that of substitution, of which we shall speak hereafter.

But the theory of radicals stood its ground. It has since even been regenerated; and the echo of these first debates had scarcely died away, when, receiving an unexpected development at the same time as its rival, it formed an alliance with the latter. Let us, however, return to the commencement, and endeavour to estimate the aid which Berzelius drew from it to crown the work which he had undertaken, namely, the introduction into organic chemistry of the ideas which prevailed in mineral chemistry. The comparison which he had established between ether and the oxides of mineral chemistry was peculiarly happy.

By assimilating alcohol to a hydrate, and compound ethers to salts, he gave the means of representing the composition of all these bodies by dualistic formulæ.

A distinction was then made in chemistry between compounds of the first order, formed by the union of two elementary bodies, and compounds of the second order, resulting from the union of two binary compounds. The oxide and chloride of ethyl, analogous to the oxide and chloride of potassium, represented compounds of the first order; the hydrate of oxide of ethyl (alcohol) and the acetate of oxide of ethyl (acetic ether) were compounds of the second order, the first being formed by the union of oxide of ethyl with water, the second by the union of oxide of ethyl with acetic acid. In all these compounds there were two elements; in their formulæ two terms. Between these formulæ and those of the corresponding compounds of potassium, there was no other difference than the substitution of the compound radical ethyl for the simple radical potassium. Analogies of the same kind were noticed in the case of other bodies: acetic acid containing acetyl and 3 atoms of oxygen was compared with sulphuric acid, which contains sulphur and 3 atoms of oxygen. This was the first attempt to inaugurate that alliance between organic and mineral chemistry which it was so desirable to cement strongly.

The edifice raised by Lavoisier had broad foun-

dations: it was able to support this beautiful superstructure. Moreover, the founder himself had foreseen this extension of his work. His idea respecting organic radicals is found again, extended and defined, in the beautiful conception of Berzelius.

But, at the time now under consideration, all chemists did not agree about the nature of organic radicals. Some, following Berzelius, excluded oxygen from these radicals; others admitted that it might form part of them. This last opinion was derived from a beautiful research, published in 1828, by two young chemists just then entering on their scientific career, and whose efforts, sometimes united, sometimes isolated, were destined to leave on chemistry a deep impression. In studying the essential oil of bitter almonds, Wöhler and Liebig discovered a certain number of compounds, exhibiting the strongest marks of relationship, on the one hand, to this essence, and, on the other, to an acid called benzoic acid, which had been extracted from benzoïn. These relations were very happily expressed by the hypothesis of a common radical existing in all these bodies, and formed of carbon, hydrogen, and oxygen. This radical is benzoyl. Oil of bitter almonds was represented as a compound of this radical with hydrogen. When this latter body is replaced by chlorine, the hydride of benzoyl is transformed into chloride of benzoyl. In contact with water, this latter body is resolved

into hydrochloric acid and oxide of benzoyl, which, remaining combined with the elements of the water, forms hydrate of oxide of benzoyl, and this hydrate is no other than benzoic acid itself. Moreover, this last-named body is likewise produced by the direct fixation of oxygen on the hydride of benzoyl, that is to say, on oil of bitter almonds. All these reactions, and others too numerous to mention, authorise the conclusion that oil of bitter almonds and its numerous derivatives contain, as it were, a common nucleus, which in them is combined with hydrogen, chlorine, bromine, sulphur and oxygen, and passes unchanged by double decomposition, from one compound to another. This double property justified the consideration of this nucleus as a radical, although it had not been isolated.*

The theory of benzoyl has made its fortune. It had the seal of a good hypothesis. It connected facts in a simple manner, and carried within itself the germ of great developments. Berzelius at first received it with favour, but afterwards rejected it, to return to his former conception of non-oxygenated radicals, which he developed to its utmost limit. Twenty years afterwards, the benzoyl theory was avenged for this desertion. We find evident marks of it in the beautiful conceptions of Williamson and Gerhardt on the constitution of acids.

* Note 4, at the end.

III.

The preceding developments show how dualism was introduced into organic chemistry by the theory of radicals. It had been firmly established in mineral chemistry by the electro-chemical theory, thanks to the efforts and the authority of Berzelius.

Berzelius was not the original author of this theory, although his researches form the experimental foundation on which it rests. The researches of Nicholson and Carlisle on the decomposition of water by the battery, and those of Cruikshank on the changes of tint produced in vegetable colours by the passage of the current, were isolated facts, when Berzelius and Hisinger made known, in 1803, the decomposing influence of galvanic electricity on a large number of chemical compounds, especially on salts. We know with what success Davy occupied himself with analogous researches, begun in 1806. The discovery of the alkali-metals was the brilliant experimental result of these researches: a novel view of chemical affinity was their theoretical consequence.

Davy supposed that bodies possessing chemical affinity for one another are in opposite electrical states, the one being electro-positive, the other electro-negative. It is by virtue of these opposite electrical tensions that they combine, and the energy of this combination, which measures the affinity, is

proportional to the degree of the tensions. The force which governs electric attractions and repulsion is, therefore, identical with that which governs chemical actions; with this difference, however, that, in the former case, it shows itself in bodies taken in mass, whereas, in the latter, it is exercised upon their smallest particles. Volta had shown that, when two metals touch one another, they develop electricity, each assuming an electrical tension opposed to that of the other. Davy pointed out that this electrical state is manifested in the contact of all bodies possessed of chemical affinity the one for the other, and that this tension is stronger in proportion as the affinities are more energetic. Combination, that is to say, the intimate approximation of the particles, is then the consequence of electric attraction. The particles, having acquired by contact opposite electrical tensions, place themselves together, and, by their union, the neutralisation of the two contrary electrical tensions is effected.

According to Davy, the heat and light developed by certain bodies in combining, are nothing but an electrical phenomenon, similar to the production of the spark: they are, in fact, the evidence of the exchange of electricities which takes place during combination. Lastly, the decomposition of bodies by the battery, restores to their elements the opposite electrical states by which they were characterised

before their union, and separates each of them at the pole of contrary name.

Such, in few words, was the first electro-chemical theory. Berzelius adopted its fundamental idea, and gave it a new form.

Reviving an idea previously suggested by Schweigger, he supposed that the atoms of all bodies have two poles, in which are accumulated quantities of electricity not always equal. According to the predominance of the one or the other electricity at each of its poles, the atom is electro-negative or electro-positive, and the quantities of electricity which thus predominate at one of the poles are far from being equal for the atoms of different bodies. In other words, the atoms of all bodies are polarised by electricity in various degrees, and this polarity may vary with the temperature.

When one body combines with another, the atoms place themselves together by their contrary poles, and thus exchange the opposite electricities there accumulated. This exchange produces a neutralisation more or less complete, and gives rise to manifestations of heat and light.

Berzelius accordingly divided the elementary bodies into electro-negative and electro-positive—negative electricity predominating in the former, positive electricity in the latter. Bodies are arranged in these two series according to the degree of this

predominance. But the electric order does not indicate the order of the affinities. Thus, oxygen, the most electro-negative of all bodies, possesses greater affinity for sulphur, its nearest neighbour in the electric series, than for gold, which is electro-positive. Berzelius explained this fact by supposing that affinity depends upon the intensity of polarisation; that is to say, on the absolute quantity of electricity accumulated at the two poles. For sulphur this quantity is much larger than for gold. The positive pole of the atom of sulphur contains a much larger quantity of positive electricity than the positive pole of the atom of gold; and, since the atoms attract one another by their contrary poles, it is evident that sulphur must exert upon oxygen a stronger attraction than gold.

We see, also, that in the case of sulphur there can be no neutralisation, since, on the one hand, the positive electricity of the sulphur-atom is not sufficient to neutralise the negative electricity of the oxygen-atom; and, on the other, this atom of sulphur brings into the combination a notable excess of negative electricity accumulated at one of its poles. The product of the combination must, therefore, be itself electro-negative. It is, in fact, a powerful acid, namely, sulphuric acid. Thus, acids result in general from the union of an electro-negative body with oxygen; bases from the union of oxygen with a

body strongly electro-positive. The alkali-metals are at the head of the electro-positive scale. Their compounds with oxygen are the most powerful of all bases, and the very strong affinity of these bases for acids is due precisely to the opposition of their electrical states and the intensity of their polarisation.

It is scarcely necessary to remark how firm a base this theory supplied for dualism. Every compound body is formed of two elements, one electro-positive, the other electro-negative. What a striking confirmation of the ideas of Lavoisier, especially of his theory of salts! You see, said the master, that salts contain the elements of the acid, placed side by side with those of the oxide, and not confounded with them: for when we subject a salt, such as sulphate of soda, to the decomposing action of the current, the sulphuric acid, or electro-negative element, goes to the positive pole, and the soda, or electro-positive element, to the negative pole. When sulphate of copper is decomposed under the influence of the current, it is not the oxide of copper that is deposited at the same pole, but the copper itself: for the oxide is then resolved into its two elements, oxygen and copper, the oxygen being liberated, together with the acid, at the positive pole. Thus, the dualistic formulæ of salts appeared to be supported, not only by the facts relating to the synthesis of these compounds, and their most ordinary mode of

formation, but likewise by the decomposition which they undergo under the influence of the electric current. We now know that this argument is unsound, and that it may be turned against the hypothesis which prevailed for so long a time respecting the constitution of salts. We know that in the electrolysis of sulphate of soda, as well as in that of sulphate of copper, it is not the oxide, but the metal, the sodium, that is carried to the negative pole, and that the free alkali appears there only in consequence of a secondary action, namely, the decomposition of water by the sodium around the negative electrode. We know that the facts relating to the uniform work of the current in saline solutions are contrary to the dualistic hypothesis, which assumes the existence of an oxide ready formed in salts.

But this was not known in 1830, and the electrochemical hypothesis of Berzelius was accepted by all chemists. The experiment of the electrolytic decomposition of sulphate of soda had become classical. It was repeated in all courses of public lectures, and invoked in favour of the ideas then so widely diffused respecting the constitution of salts.

The dualistic system was then at its apogee. And, in fact, the hypothesis of Lavoisier on the constitution of salts, which is its foundation, is so simple, and represents so well the greater number of facts concerning the modes of formation and decomposition

of salts, that it gained the mastery over all minds. It reigned in books; it was supreme in education; it gave rise to great discoveries; it had a history; and, better still, it had traditions. 'The frequent repetition of an opinion often gives rise to a conviction of its truth.' Berzelius said so, and his words may be applied to his own opinions. These opinions have reigned so long that we have insensibly become accustomed to take for demonstrated truth that which is only hypothesis. In proof of this, we may cite the general incredulity opposed to the hypothesis of Davy on the constitution of salts, a hypothesis which was adopted by Dulong, and will be explained further on. As to the ideas of Longchamp, they were met, not merely with incredulity, but with absolute contempt. And, nevertheless, Davy and Dulong were the precursors of Laurent and Gerhardt; and if we examine attentively the formulæ by which the atomic constitution of salts is represented at the present day, we shall find in them the trace of the ideas of Longchamp.*

IV.

At the time when Berzelius was beginning to acquire that authority which he exercised for so long a time, when mineral chemistry appeared complete,

* Note 5, at the end.

and all efforts tended to fashion organic chemistry in the likeness of her elder sister, a young man at Geneva was engaged in researches on various subjects of physiology, which were the precursors of discoveries destined to lead chemistry into new paths. M. Dumas was born at Alais in 1800; he was scarcely twenty years old when he published, in conjunction with Bénédict Prévost, those experiments on the blood which are regarded as classic even at the present day. Arrived in Paris in 1821, he devoted himself wholly to chemistry, and was soon in a position to undertake and publish researches of the greatest importance. The independent development of organic chemistry, and the reform of mineral chemistry by the progress thus made: such is the era which commences with Dumas. This programme was first traced by him, but it is not yet complete. Powerful auxiliaries put their hands to it with him, and after him, and among these shine in the first rank Laurent and Gerhardt, who disappeared too early from the scene, but whose names remain imperishable in the history of science. From the united efforts of these three philosophers, there has sprung a school—the new French school. Berzelius was its adversary from the very first day: Dumas was for a long time its head and its support. Well known to all is the memorable discussion in which he ventured to attack, in his most cherished ideas, the

great promoter of dualism and of the electro-chemical theory. It was Dumas who first sustained the shock, and bore triumphantly the weight of a contest, to all appearance desperate. It is right, therefore, to associate his name with the great name of Berzelius.

Among the large number of researches which he has published, we must limit ourselves to a citation of those which have exercised a decisive influence on the theoretical development of the science. Amongst the oldest we may single out those researches on vapour-densities, which have yielded to physics a new method, and to chemistry rich materials for the discussion of the hypothesis of Avogadro and Ampère.

M. Dumas' most important discoveries date from 1834. At that time he was studying the action of chlorine on various organic substances. This subject was almost new, for our knowledge relating to it was then limited to a single observation of Gay-Lussac. In examining the action of chlorine upon wax, that great chemist had discovered that the wax loses hydrogen, and takes up, for every volume of that gas thus removed, an equal volume of chlorine. Dumas made a corresponding observation respecting the action of chlorine on oil of turpentine, on Dutch liquid (1831), and afterwards on alcohol. In a memoir read before the Academy of Sciences on January 13, 1834, he expressed himself thus :—

'Chlorine possesses the remarkable power of laying

hold of the hydrogen of certain bodies, and replacing it atom for atom.'

A new thought could scarcely be expressed in more precise language. But, in the very memoir which we are considering, the author was led to formulate a restriction; for he had the rare good fortune and the merit of discovering the laws of substitution, by examining a case in which, by a remarkable exception, these laws do not come out in all their evidence. We know, in fact, that chloral, the final product of the action of chlorine upon alcohol, is not a substitution product of that body. Nevertheless, Dumas was led, by grouping together all his observations and taking account of the last, to lay down the following rules:—

1. 'When a body containing hydrogen is subjected to the dehydrogenating action of chlorine, bromine, iodine, oxygen, &c., for every atom of hydrogen which it loses, it gains an atom of chlorine, bromine, or iodine, or a half-atom of oxygen.'

2. 'If the hydrogenated body contains oxygen, the same rule holds good without modification.'

3. 'If the hydrogenated body contains water, the latter loses its hydrogen without replacement; and if, subsequently to this point, a new quantity of hydrogen be removed from the body, this hydrogen is replaced, as in the preceding cases.'

These rules are purely empirical—a point on which

Dumas strongly insists. At the time now under consideration, he desired simply to announce the fact of the replacement of hydrogen by chlorine, without preoccupying himself with the place taken by that element in the new compounds, or with the part which it plays there. Laurent first ventured to put forth the hypothesis that the chlorine in these bodies takes the place of the hydrogen, and plays the same part. He founded his opinion on the comparison of the properties of the chlorinated body with those of the original hydrogenated compound. This was an important extension of the ideas of Dumas, who at first charged it with exaggeration, but afterwards adopted it. At present, after the lapse of more than thirty years since these first discussions, we can assert, as disinterested and impartial judges, that the first idea of substitution belongs entirely to Dumas; and who will fail to recognise in such a case the power of the primitive idea, of the creative thought, of the first start? In the splendid picture which we now possess, some details have doubtless disappeared: it matters not; the fundamental lines are ineffaceable. For the rest, Laurent himself has recognised the priority of Dumas. In speaking of the composition of one of the derivatives of naphthalene, he expresses himself thus:—'This composition is sufficiently remarkable, because it fully confirms the law of substitution discovered by Dumas, and the theory of

derived radicals, of which I have already given a slight sketch.'

Such were the first steps of a theory destined to exercise a decisive influence upon chemical doctrines. It took its place in the science, slowly and with difficulty: for it offended established notions, and the most influential representative of these ideas received it with disdain. How, indeed, could the defender of the electro-chemical theory accept this idea of Laurent, that chlorine—an electro-negative element—is capable of discharging in a compound the same function as hydrogen, which is an electro-positive element? Such an assertion, put forth by a young chemist, then without authority, appeared to him unworthy of serious refutation. Afterwards, when Dumas had adopted this idea, and dealt the first blows against the electro-chemical theory, Berzelius, rightly estimating the danger, entered resolutely into the arena, and commenced a sanguinary strife against the partisans of the substitution theory. This theory had just received a splendid confirmation by the discovery of trichloracetic acid.

We know that this acid differs from acetic acid by containing three atoms of chlorine in place of three atoms of hydrogen. 'It is chlorinated vinegar,' said Dumas; 'but what is very remarkable, at least for those who refuse to find in chlorine a body capable of replacing hydrogen in the precise and com-

plete sense of the word, this chlorinated vinegar is just as much an acid as common vinegar itself. Its acid power has not changed. It saturates the same quantity of base as before, and saturates it equally well, and the salts to which it gives rise, exhibit, when compared with the acetates, resemblances full of interest and generality.

'Here then is a new organic acid containing a very considerable quantity of chlorine, and exhibiting none of the reactions of chlorine: its hydrogen has disappeared and has been replaced by chlorine, and yet this remarkable substitution has produced only a slight change in its physical properties, all its essential characters remaining unaltered.'

'If its internal properties are modified, this modification becomes apparent, only when, through the intervention of a new force, the molecule itself is destroyed and transformed into new products. . . . It is evident that, in confining myself to this system of ideas dictated by facts, I have not in any way taken into consideration the electro-chemical theories on which Berzelius has generally based the ideas predominating in the opinions which this illustrious chemist has endeavoured to enforce.

'But do these electro-chemical ideas, this special polarity attributed to the molecules of elementary bodies, rest upon facts so evident that it is necessary to erect them into articles of faith? Or, if they

must be regarded as hypotheses, have they the power of bending themselves to facts, of explaining and foreseeing them with so complete a certainty as to have afforded important assistance in chemical researches? It must plainly be allowed that this is not the case. . . '

This bold language plainly foretold the opposition which the electro-chemical theories were about to encounter—an opposition which, quickly going beyond its original object, was destined to be directed against the dualistic system itself.

Berzelius, for his own part, did not grow weary in his vigorous defence. Being unable to deny the facts, he explained them in his own way. This chlorine, which enters into organic compounds in place of hydrogen, plays therein the same part as oxygen. Being itself essentially electro-negative, it is united to positive hydrocarbonated radicals. A body which contains nothing but carbon, hydrogen, and chlorine, is a chloride. Thus, chloroform is the tri-chloride of formyl. A compound containing oxygen as a fourth element is at once an oxide and a chloride, both these being binary compounds, and forming by their union a more complex but still binary compound. Acetic acid is trioxide of acetyl combined with water; trichloracetic acid has a constitution altogether different. It is a compound of sesquichloride of carbon and sesquioxide of carbon

(oxalic acid), the whole being combined with water. Thus these two bodies, between which Dumas had pointed out the simplest relations of composition, and such evident marks of analogy, were placed by Berzelius a long distance apart.

He did the same thing with other organic bodies and their chlorinated derivatives. To these latter he sometimes assigns extremely complicated formulæ, in which several molecules of a chloride are united with several molecules of an oxide. In the construction of these formulæ, Berzelius shows himself both ingenious and arbitrary, every day inventing radicals, which he joins, sometimes to chlorine, sometimes to oxygen. As fertile in hypotheses as he had formerly been in exact analyses and in discoveries, he pushes his system to its remotest consequences, and ruins it by its very exaggeration.*

A conception, new at that time, which has given rise on several occasions to animated discussions, plays a great part in these productions of Berzelius: it is the idea that two substances, in combining together, may form a union more intimate than that in which acids and oxides are found in salts. It is observed, in fact, that, in the compounds of sulphuric acid with various organic bodies, this acid is no longer precipitated by baryta; whence it had been concluded that the union between the acid and the organic body

* Note 6, at the end.

is so intimate that one of the most important properties of the former, namely, the power of forming an insoluble compound with baryta, isdestroyed or masked.

Gerhardt designated acids of this kind as 'copulated acids;' the organic body intimately combined with the acid was the 'copula.' Dumas subsequently designated them by the more appropriate term of 'conjugated compounds.' Berzelius, after having rejected the idea, and ridiculed the word, adopted both the one and the other. He arranged in the class of 'copulated' compounds a very large number of organic bodies, the formulæ of which were resolved into two parts intimately connected one with the other. The intimacy of this union was supposed to account for the resistance which such compounds offer to double decomposition. Sulphuric acid in such compounds loses the property of precipitating baryta; chlorine can no longer be detected by nitrate of silver. The very impossibility of resolving copulated compounds into their proximate elements gave free scope to the energy of Berzelius: he multiplied at pleasure the number of 'copulas,' without taking the superfluous trouble of supporting their existence by experimental proofs.

And while this powerful intellect was exhausting itself in so profitless a labour, what was going on in the opposite camp? Discoveries. Dumas was efficiently seconded by younger men. At the head

of these stands Laurent, whose admirable researches on naphthalene enriched the science with a large number of compounds formed by substitution. An equal success crowns the beautiful memoirs of Regnault on the chlorinated derivates of hydrochloric ether and of Dutch liquid, and soon afterwards those in which Malaguti, with an exactness never surpassed, studies the action of chlorine upon ethers.

All these researches form an epoch in the history of the science; new facts come crowding together and unite in corroborating the new theory. This theory was at once rectified and extended; and, amongst its most important developments, we must particularise an idea, first suggested by Dumas, concerning the substitution of groups of atoms or compound radicals for simple bodies such as hydrogen. Nitro-compounds, that is to say, compounds formed by the action of strong nitric acid on a large number of organic bodies, were regarded as containing the elements of hyponitric acid substituted for hydrogen. Such was the origin of the ideas which afterwards became current on the substitution of compound radicals for elements, and form a dominant feature in the theory of types. The latter is the daughter of the theory of substitution, which has shown itself doubly fertile, in bringing to light, not only an immense number of facts, but likewise a new theory. Rarely has an idea given rise to so great a movement or so

great a controversy. Foreign philosophers, led on by Berzelius, at first received it with mistrust, regarding it, if not as a dangerous innovation, at all events as a superfluous development of a known doctrine. It is, said they, a particular case of the theory of equivalents; but Dumas gave to this argument an unanswerable reply;* and by degrees opposition gave way before the evidence of facts and before the authority of advocates won over to the new theory. Already, in 1839, a man who has exerted a great influence on the progress of chemistry, namely, Liebig, declared that the interpretation proposed by Dumas of the facts relating to substitution appeared to him to afford the key of a great number of phenomena in organic chemistry.† 'I do not share,' said he, 'the views which Berzelius puts forth respecting the compounds discovered by Malaguti; I believe, on the contrary, that these bodies have been produced by simple substitution.'‡ The battle was won. Berzelius himself ended by making concessions. Melsens having succeeded in converting trichloracetic acid into acetic acid by inverse substitution, that is to say, by again replacing the chlorine by hydrogen, it was no longer possible to regard these two acids as constituted in different ways. 'Then,' said Berzelius, 'they are both copulated oxalic acids; only trichloracetic acid contains

* *Comptes rendus*, viii. 600. (See Note 7, p. 202.)

† *Annalen der Chemie und Pharmacie*, xxxi. 119. ‡ *Ibid.* xxxvi. 72 (1839.)

in the copula three atoms of chlorine in place of three atoms of hydrogen.'* Thus, the substitution of chlorine for hydrogen was admitted to be possible, and to take place atom for atom, if not in organic molecules in general, at all events, in the hydrocarbonated groups which they were supposed to contain in the state of intimate combination. At length, in short, Berzelius surrendered, merely interposing an insignificant restriction for the sake of saving appearances. But, although he admitted the substitutions which he had formerly combated with so much force, he remained firm in his other convictions. The development of the theory of radicals, now strengthened by the conception of a peculiar mode of combination which they can assume in copulated compounds, enabled him to retain in the notation those dualistic formulæ which were the expression of his system. At the present day, twenty years after his death, ought our regard for his memory to make us regret the contests which agitated his latter years and from which he did not come out victorious? By no means. This great discussion has borne fruit, and the violent opposition of Berzelius has been more salutary than silence and repose could have been. Thus, after having so greatly honoured science by his discoveries, this powerful contradictor has also served it even by his errors. Such is the beneficent power of work.

* Note 8, p. 202.

LAURENT AND GERHARDT.

Among the firmest opponents of the dualistic doctrines, the history of science will always mention in the first rank Laurent and Gerhardt.

These names are inseparable, and ought to be included in a common homage, since the philosophers who have made them famous were connected together by their labours, their contests, and their friendships. Laurent and Gerhardt were of the same race, and of the same degree of importance in science. Of lofty intellect, they attacked the most difficult questions, and devoted their attention rather to points of theory than to practical applications. With different aptitudes, they pursued the same object, lending each other mutual support for the defence of the same ideas. One, an acknowledged master in the difficult art of experiment, was as skilful in discovering facts as he was bold and ingenious in interpreting them; the other, less apt for the pursuit of details, shone by his faculty of embracing phenomena in their connection. Laurent was strong in the spirit of analysis and of classification; Gerhardt was superior in the spirit of

generalisation. In the exposition of their labours which we are about to offer, we shall endeavour to trace the part of each, although their work, considered in its entirety, may be regarded as common to both.

I.

Auguste Laurent was born on the 14th of November, 1807, at La Folie, near Langres. At the age of nineteen he entered as a day scholar at the École des Mines, which he quitted three years later with the diploma of 'ingénieur.' In 1831 he was appointed 'répétiteur du cours de chimie à l'Ecole centrale des arts et manufactures.' The professor was Dumas. He received the young Laurent, and initiated him in the processes of organic analysis. Laurent at first occupied himself with determining the composition of naphthalene, which he succeeded in extracting from coal-tar. Thus, by a fortunate circumstance, he encountered at the outset that compound at once so stable and so plastic, the study of which was destined at a future time to form the favourite subject of his labours.

In a historic point of view, the compounds of naphthalene exhibit a real importance, and the ideas which Laurent put forth on their constitution in his first labours deserve to be recorded. He had stated that the solid chloride of naphthalene contains less hydro-

gen than naphthalene itself, the chlorine having removed a portion of that element in the form of hydrochloric acid. He accordingly regarded the chlorinated compound in question as the chloride of a new hydrocarbon, containing less hydrogen than naphthalene itself. The idea that a portion of the chlorine could be substituted for the hydrogen removed, and play, in the resulting compound, the same part that the hydrogen played in the original compound, did not then present itself to his mind, or, at least, was not actually expressed in this first memoir. The point of view therein developed is conformable to the theory of radicals. The naphthalene, in losing hydrogen under the influence of chlorine, is converted into a radical which unites with chlorine, to form a chloride in which the chlorine performs the same part as in a mineral chloride.

Such appears to have been Laurent's first idea.* But these views were soon modified. Two years later, adopting the idea of substitution, he arrived at a different interpretation. 'In comparing,' says he, 'the action of bromine, chlorine, oxygen, and nitric acid in various hydrocarbons, we arrive at the following conclusion, the first part of which belongs to M. Dumas:—

'1. Whenever chlorine, bromine, oxygen, or nitric acid exerts a dehydrogenating action upon a hydro-

* Note 9, p. 203.

carbon, the hydrogen removed is replaced by an equivalent of chlorine, bromine, or oxygen.

'2. At the same time there is formed hydrochloric acid, hydrobromic acid, and water, or nitrous acid, which are sometimes disengaged, sometimes remain combined in all the new radicals produced.'

These two propositions contain the germ of a theory which Laurent first enunciated in 1836, and developed in his Inaugural Dissertation, read at the Faculté des Sciences de Paris, in 1837: I mean the theory of nuclei, which here deserves a short notice, although it has played but a secondary part in the development of modern theories. Here are its principal features.

The molecules of organic bodies are either nuclei or compounds of these nuclei with other substances placed without them.

The nuclei themselves are formed of groups of carbon-atoms united with other elements, each nucleus containing a fixed number of carbon-atoms, united with a determined number of other atoms, grouped around the former according to an invariable order; and generally the number of carbon-atoms in each nucleus bears a very simple ratio to the number of the other atoms.

Nuclei or radicals are of two kinds, fundamental or derivative. The former contain only carbon and hydrogen. When they are modified by substitution, they constitute derived nuclei or radicals. The ele-

mentary bodies most frequently substituted for the hydrogen of radicals are chlorine, bromine, iodine, oxygen, nitrogen. But compound bodies, acting as radicals, may in like manner be substituted for hydrogen, and enter into the nucleus. Thus, hyponitric acid, which is anhydrous nitric acid minus an atom of oxygen; amidogen, which is ammonia minus an atom of hydrogen; imidogen, which is ammonia minus two atoms of hydrogen; arsidogen, which is arsenetted hydrogen minus an atom of hydrogen; and cyanogen itself: all these radicals indeed can replace the hydrogen of nuclei, atom for atom. It follows that to each nucleus or fundamental radical there correspond a certain number of derived nuclei or radicals. In all of them the number and arrangement of the atoms remain the same, reckoning, however, as single atoms the compound groups which play the part of simple bodies.

Other elements, such as hydrogen, chlorine, bromine, iodine, oxygen, sulphur, may group themselves around each nucleus, to form various compounds belonging to the same family. Thus, the family of ethylene, or olefiant gas, comprises, independently of this body, which is the fundamental radical, the chloride and bromide of ethylene, formed by addition of two equivalents of chlorine and bromine; an oxide, namely, aldehyde, which is formed by addition of two equivalents of oxygen; and a monobasic acid, acetic acid,

formed by the fixation of four equivalents of oxygen. The bodies formed by addition of oxygen to nuclei possess various properties, and these properties are in relation to the number of equivalents of oxygen which have been added. Aldehyde, which contains but two equivalents of oxygen, is neutral; acetic acid, which contains four, is a monobasic acid. A tribasic acid is produced by the addition of six atoms of oxygen to a nucleus. We may here direct attention to the importance of this point of view, which brought out, for the first time, the influence of oxygen on the basicity of acids. The idea was correct, but the form in which it was clothed is now no longer admissible.

Laurent remarks that these additions of chlorine, bromine, oxygen, &c., always take place by even numbers of equivalents. In no case do we see a single equivalent of these elementary bodies unite with a nucleus; it is always 2, 4, or 6 equivalents that are thus added. But, according to Laurent, the proportion of oxygen or chlorine cannot go beyond a certain limit, either within the nucleus or externally to it, without producing a kind of instability, and a marked tendency of the molecule to split up into two or more compounds belonging to lower series. It is thus that chloral is resolved, under the influence of alkalies, into a formate and chloroform.

We here see, by a new example, that Laurent not only occupied himself with the classification of bodies

according to their constitution, that is to say, according to the nature, number, and arrangement of their atoms, but that he likewise endeavoured to find in their constitution itself data for the explanation of their properties. In the thesis read at the Sorbonne on the 20th of December, 1837, he endeavoured to define, by an ingenious comparison, his ideas of nuclei, and of the atoms grouped around them as appendages.

'Let us imagine,' said he, 'a right prism with 16 faces, each of whose bases would consequently have 16 solid angles and 16 edges. Let us place at each angle a molecule (atom) of carbon, and in the middle of each edge of the bases a molecule (atom) of hydrogen: this prism will represent the primary nucleus $C^{32}H^{32}$. Let us also suspend above each base a molecule of water: we shall then have a prism terminated by summits like pyramids, and the formula of the new body will be $C^{32}H^{32} + 2HO$.

'By certain reactions it is possible, as in crystallography, to cleave this crystal, that is to say, to remove from it the pyramids, or its water, and reduce it to its primitive or fundamental form.

'Let us now bring oxygen or chlorine in contact with the fundamental radical: either of these bodies, having a great affinity for hydrogen, will remove a molecule of that element; the prism, deprived of an edge, would be destroyed if we were not to introduce in place of this an equivalent edge, whether of oxygen,

chlorine, nitrogen, &c. We shall then have a prism of 16 faces (a secondary radical), in which the number of solid angles (carbon atoms) will be to that of the edges (atoms of chlorine and hydrogen) as 32 : 32.

'The oxygen or chlorine by which the hydrogen has been removed, has united with that element, forming water or hydrochloric acid, which may either escape or be suspended in pyramids above the secondary prism. By cleavage, these pyramids may be removed; in other words, we can, by means of potash, for example, remove the pyramids of hydrochloric acid; but this alkali cannot lay hold of the chlorine which is within the prism, or, if it can, it must necessarily supply its place by another edge or another equivalent.

'Lastly, we may imagine a derived prism (radical), which, for 32 angles of carbon, should contain 8 edges of hydrogen, 8 of oxygen, 4 of chlorine, 4 of bromine, 4 of iodine, and 4 of cyanogen. The shape and formula would still be similar to those of the primary radical.'

We have here nothing left of the dualistic system. According to Laurent, the compound formed of a nucleus and its appendages, constitutes a whole, like a crystal. We see also that the theory of substitution is the basis of the system developed by Laurent, just as it afterwards served as a foundation for the theory of types, which, we may here observe, is not with-

out analogy, in its fundamental idea, to the theory of nuclei.*

Dumas, as well as Laurent, regards chemical compounds as simple edifices. Moreover, by a comparison more profound perhaps than that employed by his rival, he assimilates them to planetary systems, in which the atoms are kept in their places by affinity.

The nucleus theory is the broadest of Laurent's conceptions. It affords the means of grouping together a large number of organic compounds, and its author took care not to forget or neglect so precious a means of classification. He arranged bodies in series—an important notion, which now makes its appearance for the first time. A series embraces all bodies containing a certain primary radical or one of its derivatives. But amongst all these bodies there are distinctions to be made. Although they possess in their composition a common stock, they may yet differ by the nature of the radical, which is either primary or secondary, and also by the number and kind of the atoms added to it. They differ, therefore, by the type to which they belong, and naturally also by the functions which they are adapted to discharge. Hence the possibility of establishing for each series a certain number of types which are reproduced in all the others. In the creation of types, Laurent showed himself both acute and fertile—too fertile, perhaps.

* Note C, p. 218.

If some of these types, which mark the functions of compounds have survived, others have fallen into oblivion. At the present day we still talk of anhydrides, amides, imides, amidated acids, aldehydes; but who cares to remember analcides, halydes, camphides, protogenides, &c.? The words have disappeared from scientific language, because the things which they denoted were not worthy of preservation.

Laurent's classification, the bases of which we have just recapitulated, was therefore nothing but an ingenious experiment, just as his nucleus theory was only a premature effort. It is true that Leopold Gmelin, a man great by his erudition and the independence of his judgment, has made it the foundation of his celebrated 'Handbook of Chemistry;' but he has not succeeded in bringing it into general use.

Another theory, which arose about the same time, has had this good fortune. It was at first limited, like the theory of nuclei, and in perfecting the latter, Laurent borrowed certain features from the other. Moreover, both these theories rested on the same base, namely, the theory of substitution, but the one carried within itself the germ of important development: we mean the theory of types, which we shall presently have to explain.

After having endeavoured to trace the important part played by Laurent in the theory of substitution,

and his strife with dualism, in which he was a powerful auxiliary to Dumas, we have in the preceding observations recalled the grand conceptions which are his own.

These, however, are not the only services which Laurent rendered to science. His labours formed a pupil who alone was worth a whole school, and has himself become a great master. The young Gerhardt was attached by friendship to Laurent, whose ideas he had adopted. Afterwards he lent him his own ideas, their parts being to a certain extent reversed. It would, therefore, be unjust to place either of them below the other.

II.

Charles-Frédéric Gerhardt was born at Strasbourg, on the 21st of August, 1816.

He soon gave proof of a distinguished mind and independent character. After a somewhat unsettled youth, he devoted himself to the study of chemistry under the auspices of Liebig, at Giessen, where that great master, then in the first blaze of his renown, attracted young philosophers from all parts of the world, and founded a justly celebrated school.

In the first steps of his career, Gerhardt displayed the measure of his powerful faculties. He was more skilful in seizing the general aspect of a question than in following out its details by way of experiment.

An acknowledged master in the art of grouping and interpreting facts, he drew from them consequences of the highest importance and the greatest utility for theory. If Laurent excelled in measuring and sifting phenomena by the finest analysis, Gerhardt possessed in a higher degree the spirit of system, and, as it were, a general intuition into things. He commanded his subject.

On the 5th of September 1842, he read at the Academy a memoir, entitled: *Recherches sur la classification chimique des substances organiques*, in which he put forth new and important views respecting the equivalents of carbon, hydrogen, and oxygen. These views he afterwards developed in a more extended work. They are founded on the following fact: When an organic reaction gives rise to the formation of water or of carbonic acid, the proportion of these bodies never corresponds with what was then called an equivalent, but always with two equivalents or a multiple of this quantity. Gerhardt was struck with this fact, which appeared strange to him, and seemed to betray some error, either in the determination of the molecular size of organic bodies, or in that of the equivalents of carbonic acid and water, or rather of carbon and oxygen. In fact, it was impossible to admit that no reaction whatever of organic chemistry could give rise to a single molecule of water or of carbonic acid. 'Of two things, then,' said he, 'one

must be true,* either H^4O^2 and C^2O^4 represent single equivalents, or each of them represents two.' On the former supposition, it would be necessary to double the formulæ of mineral chemistry, 'in order to make them agree with organic formulæ:' this is what he first proposed to do. On the other hypothesis it would, on the contrary, be necessary to reduce all organic formulæ to one-half. It was this last device that he finally adopted.

These organic formulæ thus reduced are the atomic formulæ of Berzelius. Following the example of that chemist, Gerhardt regards water as formed of 2 atoms of hydrogen and 1 atom of oxygen. He returns, therefore, as regards hydrogen and oxygen, to the atomic weights of Berzelius, as also for carbon and nitrogen, that is to say, for the ordinary elements of organic compounds. With the English chemists, he refers these atomic weights to that of hydrogen taken as unity.

He then shows how Berzelius was led to attribute to most organic bodies formulæ double of those which really express the composition of their molecules. He reminds us that the acids were the bodies whose 'equivalent,' that is to say, molecular weight, was determined in the first instance. For this determination the great Swedish chemist had recommended the analysis of their salts, those of lead and silver for

* *Précis de Chimie organique*, i. 49.

example. The equivalent of an organic acid was, in his view, the quantity of acid combined with a quantity of silver oxide containing one equivalent of silver. But Berzelius had taken for the equivalent of silver a number double of that which is rightly assigned to it. Consequently, the equivalent, that is to say, the molecular weight of the organic acid, came out twice as great as it ought to be. This remark applies especially to the monobasic acids, such as acetic acid. But it is immediately seen that the formulæ of the most various organic compounds must have been affected with the same irregularity. Thus, the formula of acetic acid having been doubled, it became necessary to double that of alcohol, as well as of most of the compounds related to it.

But on what argument did Gerhardt rely for the assumption that the atomic weight of silver, as admitted by Berzelius, was twice as great as it ought to be?

He was guided by the analogy often remarked between protoxides and water. 'If water,' said he, 'contains two atoms of hydrogen and one atom of oxygen, oxide of silver must have a similar constitution. For 1 atom of oxygen it must contain two atoms of silver, and the weight of one of these atoms must be the half of that which Berzelius attributed to the equivalent of silver in the oxide, formed, according to his views, of one equivalent of silver and one equiva-

lent of oxygen. This point of view was extended by Gerhardt, not only to the alkaline oxides, but likewise to protoxides in general. The atomic weights of the metals were, therefore, reduced by one half.

The notation founded on this new system of atomic weights led to formulæ rigorously comparable amongst themselves. Gerhardt rightly observes, that the double formulæ of organic compounds, as constructed by Berzelius, were far from corresponding with the formulæ of the greater number of mineral compounds. Those of acetic acid and alcohol, corresponding to four volumes of vapour, were not comparable with that of water, which corresponds to two volumes. Reduce then the former to one half, and they will express two volumes of vapour, like the formula of water. The meaning of this language is easily understood. When we say that a molecule of water occupies two volumes, we express, strictly speaking, nothing more than the ratio of the volume of this molecule of water to that of an atom of hydrogen supposed to occupy a single volume, or the unit of volume.

Laurent and Gerhardt insisted strongly on this point. The molecules of compound bodies are formed of the atoms of simple bodies kept together by affinity; they differ from one another in size and in weight according to the number and the nature of these juxtaposed atoms. For each compound body a molecule is the smallest quantity that can exist in the free

state, or that can enter into a reaction, or be produced therefrom. All the molecules of any one compound body are similar to one another. The molecules of one compound body differ from those of another by the number and nature of their elementary atoms, or, to speak more generally, by their magnitude. As the magnitudes of molecules can only be determined relatively, it is necessary to choose a *unit* of molecule, to which the molecules of all compound bodies can be referred, just as a unit of atom is chosen, namely, that of hydrogen, with which all others are to be compared. According to Gerhardt, all bodies and all reactions should have a common measure. On this condition alone can the relative sizes of their molecules be fixed with rigorous exactness.

This common measure for the determination of molecular magnitudes is the molecule of water. With this it is convenient to compare the molecules of all other bodies, which like it should, in the state of gas or vapour, occupy two volumes.

This is one of the most important points of Gerhardt's doctrine; it rests in a general manner on a truly logical development of the theory of volumes: molecular magnitudes being rigorously deduced from the consideration of volumes, molecular weights determined by the comparison of the weights of equal volumes of gases or vapours, that is to say, by the density of these gases or vapours. This point of view was not restricted to organic compounds. Gerhardt

has extended it to the most varied mineral compounds. Thus, the molecule of ammonia no longer contains, as Berzelius had supposed, 2 atoms of nitrogen and 6 atoms of hydrogen, occupying 4 volumes; but it is formed of 1 atom of nitrogen and 3 atoms of hydrogen, and occupies only 2 volumes. In like manner, the molecule of hydrochloric acid, which is formed of only 1 atom of hydrogen and 1 atom of chlorine, occupies only two volumes. This is the quantity which is comparable with a molecule of water, and not the double quantity, as supposed by Berzelius. Metallic chlorides are related to metallic protoxides in the same manner as hydrochloric acid is related to water, that is to say, they contain only a single atom of chlorine joined to a single atom of metal.

From these considerations there has been deduced a system of formulæ differing both from that of Berzelius, and from the equivalent notation subsequently adopted; and this new mode of formulation could not, with regard to a large number of compounds, be reconciled with dualistic ideas. This is an important point, which it is useful to bring to light.

Sulphate of silver is supposed by Gerhardt to contain 2 atoms of silver. Hydrated sulphuric acid, being in fact bibasic, contains 2 atoms of hydrogen replaceable by 2 atoms of metal, or, according to the theory of dualism, it contains a molecule of anhydrous sulphuric acid united with a molecule of water. In

the sulphates this molecule of water is replaced by a molecule of base; that of silver contains, therefore, the elements of anhydrous sulphuric acid together with those of oxide of silver. This oxide Gerhardt supposes to contain 2 atoms of silver: these are found also in the sulphate, and the formula which he attributes to this salt agrees, as respects molecular magnitude, with the dualistic formula, in this sense —that, like the latter, it contains, though without determinate grouping, all the elements required to constitute a molecule of anhydrous acid and a molecule of oxide.

But it is otherwise with acetate of silver. The formula assigned by Berzelius to this salt represented one equivalent of acid and one equivalent of oxide. The halved formula of Gerhardt, containing only one atom of metal, made it no longer possible to regard the acetate of silver as containing oxide of silver; for one 'equivalent'* of this oxide contains, according to Gerhardt, 2 atoms of silver. In other words, the single atom of silver in the acetate could take, to form the oxide, only a half-atom of oxygen and could yield only a half-equivalent of silver oxide, a result inadmissible and irreconcilable with the dualistic theory of salts. This theory, in fact, supposes that each molecule of a salt contains an entire molecule of

* Gerhardt made use of this word, here signifying molecule, and then regarded by him in this sense.

acid and an entire molecule of base. The same remark would apply to all salts formed by monobasic acids, such as the nitrates and chlorates. Gerhardt could no longer regard them as constituting binary molecules, double edifices as it were.

Generalising the views proposed by Dumas and Laurent on the subject of organic compounds, Gerhardt regarded the salts in question, and in general all the salts, acids, and oxides of mineral chemistry, as constituting single molecules, formed of atoms some of which might be exchanged by way of double decomposition. To the dualistic point of view, he opposed the *unitary* system; to the idea of combinations resulting from *addition* of elements, he opposed that of compounds formed by *substitution*. An acid is a hydrogenated body, the hydrogen of which can be easily exchanged by double decomposition for an equivalent quantity of metal. From this exchange there results a salt. What is the change which takes place when nitric acid acts upon potash? The atom of potassium in this base, which is a hydrate, goes to take the place of the atom of hydrogen in the nitric acid; the products thus formed are nitrate of potassium and water: for the hydrogen, which has left the nitric acid, is necessary and exactly sufficient to form water with the elements of the hydrate of potassium, from which the potassium has been separated. The change which has taken place is,

therefore, a double decomposition; two molecules have entered into the reaction, namely, nitric acid and hydrate of potassium; two new molecules have resulted from it, namely, nitrate of potassium and water. With acetic acid and oxide of silver the case is slightly different; this oxide contains 2 atoms of silver and only 1 atom of oxygen: consequently 2 molecules of acetic acid must intervene in the formation of silver acetate. Each of these molecules gives up one atom of hydrogen to the oxygen of the silver oxide, to form water; and the two atoms of silver, separating one from the other, go to replace the hydrogen in the two molecules of acetic acid, thereby forming two molecules of silver acetate. From all this, it follows that acids and salts exhibit the same constitution—the former being salts of hydrogen, the latter salts of metal.

Such is the theory of Gerhardt on the formation and constitution of salts. We see in it the trace of ideas formerly put forth by Davy and Dulong, which are so important that it is necessary to recall them in this place.

In 1815 the great English chemist published a memoir on iodic acid, in which he threw out the opinion that the acid properties of this body are related to the hydrogen which it contains, in this sense, that the hydrogen may be replaced by a metal. 'Hydrogen,' said he, 'plays an essential part in the

formation and constitution of acids; it is this element which converts iodine into hydriodic acid; and it, likewise, brings to the state of acid 1 equivalent of iodine and 6 equivalents of oxygen, which in iodic acid are united with 1 equivalent of hydrogen. In chloric acid, it discharges a similar function.'

In a memoir on the chlorates, Davy had pointed out that chlorate of potassium is a neutral salt, and that, in giving up all its oxygen, it is converted into another neutral salt—the chloride of potassium. According to his view, the oxygen in the chlorate is not divided between the chlorine and the potassium in such a manner as to constitute an anhydrous oxide and an acid. The chlorate of potassium does not contain two proximate constituents; it contains three elements—potassium, chlorine, and oxygen—grouped together in such a manner, that the potassium takes the place occupied by the hydrogen in chloric acid.

Dulong adopted these ideas of Davy, and added to them the feature that oxacids possess a binary constitution analogous to that of hydracids. Like the latter, they contain hydrogen; but this element is united in them, not with an elementary body but with an oxygenated radical, which plays the part of an elementary body. This opinion was published in 1816, in a memoir on oxalic acid. It is known that oxalate of silver, when subjected to a moderate heat, is quickly resolved into carbonic acid and metal, and

that the composition of all the neutral oxalates in the dry state is such as to represent carbonic acid united with a metal. Dulong supposed that oxalic acid is carbonic acid to which hydrogen has been added, and that, in the formation of oxalates, this hydrogen unites with the oxygen of the oxides to form water, and is replaced by the metal. He observes, moreover, that this view may be applied to all oxygenated acids, which he assimilates to hydracids. If the latter contain a strongly electro-negative elementary substance combined with hydrogen, the former contain an oxygenated group, playing the part of a radical united with hydrogen. Liebig, in his celebrated memoir on polybasic acids, has developed the same view, and has pointed out that the affinity of acids for oxides may be due to the powerful affinity of the hydrogen of the acid for the oxygen of the oxide, the formation of water, in the cases under consideration, always accompanying the formation of salts.

Gerhardt then adopted ideas which had been enunciated before him; but he made them his own, not only by modifications introduced into the notation, but likewise by the very character of his definitions, and by his unitary formulæ. A salt is no longer to be regarded as a binary compound containing an oxygenated radical on the one side and a metal on the other; it is a whole, a single

group of several atoms, amongst which are one or more atoms of metal, capable of being exchanged for other metallic atoms or for hydrogen.

How are these atoms grouped in the molecule of the salt? Into this question Gerhardt does not enter, for he does not believe it to be capable of solution. 'It is supposed,' said he, 'that salts contain the elements of an acid and those of an oxide ready formed, and this opinion is based on the fact that many salts are formed by the direct union of an anhydrous acid with an oxide. The argument is fallacious, for there is nothing to prove that the atomic grouping of the combining elements remains unchanged after combination; this is a pure hypothesis.' According to Gerhardt, the arrangement assumed by the atoms in a complex compound is inaccessible alike to experiment and to reasoning. It is, therefore, a vain attempt to seek to define bodies according to their constitution; all that can be done is to class them according to their functions and their transformations. To express these transformations correctly, it is sufficient to represent the composition of bodies by unitary formulæ, rigorously comparable, and conveying an exact idea of molecular magnitude. The atomic movement which determines the metamorphoses of bodies may then be represented by equations containing such formulæ.

Without denying the services which may be ren-

dered by rational formulæ, Gerhardt points out their defects, and proscribes the use of them. According to him, such formulæ may express reactions, but by no means the atomic grouping of the elements of a compound. One and the same substance may undergo various transformations; consequently several rational formulæ may be assigned to it. This indeed frequently happens, as in the case of alcohol, for which six or seven different formulæ have been proposed, each author endeavouring to support by numerous reactions his own formula, which he considers the best, as if one could give the least idea of the grouping of the molecules in a compound by placing such and such a symbol on the paper, a little more to the right or to the left.* In Gerhardt's view, then, rational formulæ are hypotheses, and he inveighs with force against the abuse which Berzelius has made of them in organic chemistry. These complicated expressions, in which we see hypothetical radicals without number united with oxygen or chlorine, according to the electro-chemical rule, appeared to him destitute of foundation and probability. 'Let any one show us a single one of these radicals,' cried he, denying with conviction the possibility of their existence. In his ardour he even goes so far as to despoil cyanogen and cacodyl of their character of compound radicals. Moreover he adapts his nomenclature to his

* *Précis de Chimie organique*, i. 12.

ideas. The body resulting from the action of chlorine on bitter almond oil is not chloride of benzoyl, but chlorinated benzoïlol, a name which, as well as the unitary formula, indicates the relations of composition of the chlorinated body to bitter almond oil or benzoïlol, from which it is derived by substitution.

Thus, in this first stage of his scientific career, Gerhardt admits neither rational formulæ nor radicals, this word being taken in the sense of groups of atoms having an independent existence and the power of entering directly into combination. But the advocate of unitary ideas was too clear-sighted not to perceive that, in a large number of reactions, when compound bodies have lost one or another of their elements, the residues, which are as it were the ruins of the molecule, are capable of entering into combination. This is what he calls *substitution by residues*. The idea had been suggested by Laurent (p. 87), and was adopted by Gerhardt. It has since received many beautiful developments, and has become, in a measure, the connecting link between the theory of substitution and that of radicals, itself developed and regenerated. These residues, which Gerhardt admitted, are, in fact, nothing but radicals in the modern sense of the word.

But in 1842, Gerhardt had not reached this point. Borne on by his opposition to the doctrines then prevailing, and by the confidence inspired by his own

ideas, he did not escape the danger of exaggerating their consequences. In his *Précis de Chimie organique*, which is the first cast of his ideas, and the first evidence of his strong originality, he takes empirical formulæ for the sole basis of a new classification. He ranges all bodies in an ascending progression, according to the number of carbon-atoms contained in their molecules, the simplest compounds forming the base, and the most complex the summit of this scale. He calls it a scale of combustion, because oxidation-processes cause a body to descend in the series by one or several ranks, by depriving it of one or more atoms of carbon.

This principle of classification is excellent, but in this first attempt, Gerhardt applied it too absolutely. By relying solely on empirical formulæ he was led to make unfortunate associations: thus acetate of ethyl accompanies butyric acid; succinic acid, ethyl-oxalic acid and oxalate of methyl, follow one another closely; and adipic acid elbows oxalic ether.

Too rigorous an order produced therefore a certain confusion, which Gerhardt subsequently learned to avoid; but the habit which he had acquired of grouping bodies according to their composition, and comparing together their empirical formulæ has nevertheless borne fruit: it has contributed to introduce into the science a new and fertile idea, that of the *homologous series.*

Schiel, a German chemist, first observed the relations of composition existing between the alcohols; after him Dumas constructed the series of fatty acids, beginning with the most simple of all organic acids, namely, formic acid, and rising by a regular gradation up to the complex acids extracted from tallow and wax. Gerhardt developed this idea and fortified it by new examples. In the series which he calls homologous, bodies are ranged according to the regular progression of the atoms of carbon and hydrogen, the other atoms remaining constant, and each term differing from that which immediately precedes or follows it by addition or subtraction of CH^2. Gerhardt adds that homology results not from relations of composition alone, but also from similarity of chemical functions. Thus he has fixed the idea and created the word. Through his efforts the doctrine of homologues has become one of the most firmly established bases of the classification of organic substances.

The labours which we have just sketched in broad lines have left a deep impression on the science, and constitute, in great part the basis of our modern ideas. A new system of atomic weights founded on a logical development of the theory of volumes and on a sound appreciation of analogies; a notation in which all formulæ and all reactions are rendered comparable by a more exact determination of the

relative magnitudes of molecules; chemical compounds regarded as groups of atoms forming a single whole, a simple edifice, and capable of modification by exchange of one element for another: these are the principal features of a doctrine which, at the time of which we are speaking, was already being consolidated and beginning to gain strength. But between this first consolidation and the final triumph a long interval was destined to elapse, and the doctrine itself to undergo important modifications.

III.

Berzelius was no more. The theory of substitution had prevailed, but the developments evolved from it by Laurent and Gerhardt encountered fierce opposition. The partisans of the radical theory had accepted the fact of substitution, but still maintained a hostile attitude. Dualism was always face to face with the unitary idea. In fact, the latter, in the hands of Laurent and Gerhardt, had been an instrument adapted rather to correct errors than to lead to great discoveries. The theory flourished, but experiment rather flagged. Now, in the experimental sciences a new doctrine never makes its way by criticism alone. To secure its triumph it requires a halo of discoveries. In the present case this sanction has not been wanting. From the year 1849 various

researches followed one another, which strongly excited the attention of chemists and directed Gerhardt himself into new paths: we allude to the discovery of the compound ammonias by Wurtz and that of the mixed ethers by Williamson.

These labours brought about a reconciliation between the theory of radicals and that of substitution, —which theories, rivals till then, were amalgamated into a new theory—the theory of types. But to understand the origin and scope of this theory, it is necessary to go back for some time.

In 1839 Dumas discovered chloracetic acid. This acid is derived from acetic acid by the substitution of three equivalents of chlorine for three equivalents of hydrogen, all the other elements remaining the same. But what is very remarkable, this introduction of chlorine into the molecule does not produce any deep modification in the fundamental properties of acetic acid. Its chlorinated derivative is, like itself, a monobasic acid, capable of undergoing analogous decompositions under the influence of certain reagents. These facts, according to Dumas, admit of but one explanation: the chlorine, when substituted for the hydrogen in acetic acid, takes the place of that element, and *plays the same part* in the new compound. This he expresses by saying that acetic acid and chloracetic acid belong to the same *chemical type*. He further supposes that the properties of a

compound depend less on the nature of the atoms which it contains than on their grouping and position in the molecule.

These ideas are conformable to those put forth by Laurent himself, but, being supported by new and important facts, they possessed greater authority. Moreover, the idea of the conservation of the type after the substitution of one element for another, in a given compound, was thereby enunciated more clearly than by Laurent in his theory of nuclei.

Dumas then ranged in the same *chemical type* all bodies containing the same number of 'equivalents' grouped in the same manner, and likewise possessing the same fundamental properties. But he further observes that these properties may be modified by the act of substitution.

Bodies containing the same number of equivalents but differing by their fundamental properties, may be grouped in the same *mechanical type*. It is right to add, that Regnault, in his remarkable researches concerning the action of chlorine on Dutch liquid and hydrochloric ether, had already directed attention to the conservation of the atomic grouping by the fact of such substitutions.

It is thus that the idea of types was introduced into chemical science. But under this first form it was not susceptible of large developments. Confining itself to expressing in a precise and elegant manner

the relations created by substitution between a given compound and its derivatives, it admitted as many types as there are compounds capable of being modified by substitution, and it left these latter without any connection. Hence, though a true and ingenious idea, it did not seem destined to extend into a general theory. It has, however, become such by being modified.

For a long time, chemists, struck by the fact that all the natural alkaloïds contain nitrogen and yield ammonia by dry distillation, had foreseen the existence of intimate relations between the 'volatile alkali' and the organic alkalis. More lately, the grand discovery of the amides, due to M. Dumas, gave rise to another mode of viewing these bodies. The alkaloïds were supposed to contain, as a common element, the generating principle of the amides, which is called *amidogen*, and consists of ammonia deprived of an atom of hydrogen.

This important question of the constitution of the organic bases has been illuminated by the discovery of a class of bodies exhibiting the most striking relations of composition and properties to ammonia, the same tendency to unite with acids, the same causticity, the same solubility in water, the same odour. In announcing the existence of these 'compound ammonias,' the author expressed the opinion, that they may be regarded either as ether in which

the oxygen is replaced by amidogen, or as ammonia in which an equivalent of hydrogen is replaced by an equivalent of an alcohol-radical.* The idea of comparing them with ammonia regarded as a type, was, therefore, enunciated in this first communication, and, in fact, forced itself upon the mind by a surprising analogy of properties. Some months afterwards, Dr. Hofmann, guided by his brilliant discovery of diethylamine and triethylamine, gave greater force to the idea of types, and rendered it triumphant, by regarding all these bases as ammonia, in which one, two, or three atoms of hydrogen are replaced by one, two, or three alcoholic groups or radicals.†

Thus, then, the type ammonia was created: for it was easy to extend to the other alkaloïds—and chiefly to the volatile bases, the preparation of which by synthetical processes had already been discovered—the point of view which adapted itself so easily to the ethylated bases. We may observe, also, that the theory of substitution took possession of the radicals. Ethylamine was no longer regarded as a binary compound of ethyl and of amidogen, but as ether, the oxygen of which is replaced by amidogen, or as ammonia, in which the radical ethyl is substituted for hydrogen. Here the word radical is used in the

* *Comptes rendus*, xxviii. 224; February 1849.

† See note 10, p. 203.

sense of a group of atoms capable of combining with other atoms by way of substitution. There is no longer any question of perfectly isolated radicals ready to form binary combinations by way of addition, affecting, in a word, the behaviour of elementary bodies; they are, rather, Gerhardt's residues, which pass unaltered from one combination to another. But in so doing they do not get mixed up with the mass of the elements, but retain in the molecule a determinate place, and a distinct individuality marked by the formula itself. This formula is no longer an isolated expression. It is a rational formula, clearly indicating the relations of composition of the new bases to ammonia. Thus, at the very moment when the theory of radicals and that of substitutions were about to be fused together in the theory of types, rational formulæ were restored to honour, as a means of expressing the relationships of bodies.

A new impulse was thus given, and a new discovery helped to accelerate the movement. In 1851 Williamson published his beautiful researches on etherification and the existence of mixed ethers—researches which introduced into chemistry the water-type.

Laurent had formerly compared with water the anhydrous oxide of potassium and caustic potash. He had indicated by abridged and ingenious formulæ the relations of composition existing between alcohol

and ether.* His ideas were developed with talent by an American chemist, Mr. Sterry Hunt.

Williamson went further: he compared with water, not only alcohol and the ethers, but likewise the acids, oxides, and salts of mineral chemistry. Water being formed of one atom of oxygen and two atoms of hydrogen, it is possible to replace these latter, either by the atoms of other elementary bodies, or by groups performing the part of radicals. Replace in a molecule of water one atom of hydrogen by an ethylic group, and you will have alcohol; and if the second atom of hydrogen be likewise replaced by ethyl, the product will be ether. Potash represents water in which one atom of hydrogen has been replaced by potassium; replace the other atom of hydrogen by an acid radical, and this double substitution will give rise to a salt. Thus acetate of potassium is derived from a molecule of water by the substitution of one atom of potassium for one atom of hydrogen, the other hydrogen atom being replaced by the radical acetyl. Williamson even foresaw the existence of a body derived from water by the substitution of two acetyl groups for the two atoms of hydrogen, and bearing to acetic acid the same relation that ether bears to alcohol. This body is acetic anhydride, which was afterwards discovered by Gerhardt.†

* Note 11, p. 203. † Ibid.

All these bodies belong to the same type. They all contain one atom of oxygen and two other elements, simple or compound, representing the two hydrogen atoms of the water. Throughout all these substitutions which the molecule may experience, its skeleton remains, to a certain extent, the same, and exhibits the relatively simple structure of a molecule of water.

Such are the ideas put forth by Williamson. At the time when Gerhardt was induced to adopt them, the water-type was already made, as well as the ammonia type. Gerhardt, giving fertility to an idea which had germinated before him, added the hydrogen type and the hydrochloric acid type. He moreover gave a new extension to the water-type by his beautiful discovery of the anhydrous organic acids.

He had formerly denied the existence of anhydrides derived from monobasic acids, and had the singular good fortune to discover them himself. By making the chloride of the radical acetyl act upon acetate of sodium, he actually obtained the acetic anhydride whose existence had been foretold by Williamson. This body contains two acetyl groups united with a single atom of oxygen. Just as water contains two hydrogen atoms united with a single atom of oxygen, so likewise do the two acetyl groups or radicals of acetic acid play, in acetic anhydride,

the part of a simple body, occupying therein the place which the two atoms of hydrogen occupy in a molecule of water. It is thus that the water-type, created by Williamson, was enlarged by Gerhardt, who generalised the idea of types.

With Laurent, he regarded the molecule of hydrogen as formed of two atoms. In the free state, said he, this gas constitutes the hydride of hydrogen; free chlorine is the chloride of chlorine; free cyanogen the cyanide of cyanogen. And since oxides exhibit a constitution analogous to that of water, the molecules of metals may be compared with hydrogen; they are formed of two atoms. The hydrogen type, therefore, includes all the metals. In organic chemistry many compounds exhibit the same binary composition. Their molecules are double, that is to say, formed of two distinct elements, either simple or compound, and each equivalent to one atom of hydrogen.

Gerhardt accordingly ranged in the hydrogen type the aldehydes, the ketones, and a large number of hydrocarbons; amongst others, the alcohol radicals —ethyl and methyl—which were discovered by Kolbe and Frankland, and had been the object of animated discussions. It is a remarkable circumstance, that the partisans of dualism had regarded these bodies as single groups, while the defender of the unitary idea has shown that they result from the union of

two alcoholic radicals, and has assigned to them a binary constitution or double formula.

The hydrochloric acid type comprised the chlorides, bromides, and iodides, mineral and organic; in fact, it was identical with the hydrogen type.

These were new ideas. The following is an important development. The volatile organic bases were at first the only known bodies belonging to the ammonia type. Gerhardt included in it all the amides. Acetamide, according to him, exhibits the same molecular constitution as ethylamine, differing from the latter only by the oxygenated nature of its radical. If ethyl is a neutral radical, acetyl is an acid radical, because it contains oxygen. Acetyl, like ethyl, may be substituted for the hydrogen of ammonia; but the body resulting from this substitution is neutral, because the basic properties of the ammonia are neutralised by the introduction of an acid radical into its molecule.

Thus, bodies having a perfectly similar constitution, and, therefore, belonging to the same molecular type, may, nevertheless, differ considerably in their properties, according to the nature of the elements which occupy a given place in the molecule. This is an important proposition, indicating a return towards ideas which had formerly been attacked, at the time when a predominating influence was attributed to atomic grouping in the manifestation of properties.

To express in a striking manner this influence of the nature of the elements on the properties of bodies exhibiting in other respects the same constitution, we may, with Gerhardt, arrange on the same horizontal line all bodies belonging to the same type, the basic compounds occupying the left extremity, while the neutral bodies are placed in the middle, and the acids to the right. Take, for example, the water type. Potash, which is a powerful alkali, will be placed on one side, nitric and acetic acid on the other, water and alcohol in the middle. Why are those bodies which occupy the left extremity strongly basic? Because they contain a strongly electro-positive metal, such as potassium. Those which occupy the middle are neutral, because they contain indifferent elements or radicals; but those which are placed to the right are acid, in consequence of the oxygenated radicals which they contain.*

According to the theory of types, alcohol is water in which one atom of hydrogen is replaced by the hydrocarbonated group ethyl: this group is basic, but its basic power scarcely exceeds that of hydrogen: consequently, alcohol is a neutral liquid, like water itself. But suppose an atom of oxygen to be introduced into the molecule of alcohol, and to take the place of two atoms of hydrogen in the radical ethyl;

* Note 13, p. 204.

the radical, thus modified by substitution, will assume an acid character, and will impress this character upon the entire molecule. By this substitution nothing is changed in the molecular grouping. The two bodies exhibit the same constitution, one being the hydrate of ethyl, the other the hydrate of acetyl; but whilst alcohol is neutral, the acetic acid resulting from its oxidation is a powerful acid. Such is the influence which the nature of the atoms exerts on the properties of molecules otherwise resembling one another in the grouping of their atoms. This influence is still more evident in bodies belonging to the ammonia type. Ammonia is a strong base, and when in this molecule, formed of nitrogen and hydrogen, the hydrogen is replaced by neutral hydrocarbon groups, such as methyl or ethyl, the basic power is preserved. We know that the compound ammonias resulting from such substitutions are strong bases like ammonia itself. But the hydrogen of this latter body may be replaced, wholly or in part, either by an electro-negative element like chlorine or bromine, or by an acid radical; the derivatives of ammonia thus formed are neutral or even acid, as in the following examples.

Aniline is a powerful base; trichloraniline, or trichlorinated aniline, is, according to Hofmann, a neutral body, that is to say, incapable of combining with acids. In like manner, as we have already

observed, the basic character of the ammoniacal molecule is effaced in acetamide by the acid nature of the oxygenated radical which is therein substituted for hydrogen.

Most amides are neutral like acetamide, but we are acquainted with a few which are decidedly acid. Gerhardt, in one of his most beautiful memoirs, has described amides resulting from the substitution of two oxygenated radicals for two atoms of hydrogen in ammonia, and in which, owing to the preponderating influence of these oxygenated groups, the character of the ammoniacal molecule is modified to such a degree that it forms salts, not with acids but with bases.*

The preceding developments afford an answer to one of the objections which have been raised against the theory of types. Lavoisier, it was said, insisted so strongly on the fundamental differences between acids, oxides, and salts. Is it allowable to confound these bodies together, as is done in the theory of types? What! is it possible that caustic potash and hypochlorous acid, so dissimilar in their properties, can be cast in the same mould, and, what is more, assimilated to hypochlorite of potash, the product of their combination?

The fact is, that these bodies may be compared together without being actually confounded.† They

* Note 12, p. 204.

† Note 13, p. 204.

are distinguished by their properties, assimilated by their atomic constitution. These two points of view are totally different. Lavoisier insisted on the first when he opposed oxides to acids. The second he was unable to approach, because in his time the atomic theory was not yet born; he could not, therefore, occupy himself with the grouping of atoms. Every one will allow that compound bodies containing atoms grouped in the same manner may possess different properties if these atoms differ among themselves.

Do we confound hypochlorous acid with caustic potash, when we say that these two bodies contain an equal number of atoms grouped in the same manner, but that the one contains chlorine just in the place where the other contains potassium? Does not this fundamental difference in their composition explain the opposition of their properties? They do not, in fact, differ from one another more than chlorine differs from potassium.

The objection just discussed is therefore without weight. Kolbe has raised another and a more important one, for it seems to go to the root of the matter. 'Your three or four types,' said this chemist, 'are nothing but a vain artifice. Why are we to suppose that nature has restricted herself to forming all bodies on the models of hydrochloric acid, water, and ammonia? Why on these models rather than

upon others? To consider only organic bodies: would it not be more rational to refer them to carbonic acid? It is, in fact, from this gas that they are formed in the vegetable kingdom. The carbonic acid type must therefore exist in the very nature of things, and it seems logical to refer all organic compounds to this type, since they are all in fact derived from it.'

To this it may be replied, in the first place, that water and ammonia are agents as indispensable as carbonic acid in the processes of vegetable life. To assimilate hydrogen and nitrogen, plants must decompose water and ammonia, just as they decompose carbonic acid to assimilate carbon. This great work of the elaboration of organic matter requires, therefore, the concourse of three mineral compounds, and if we would base the idea of types on the question of origin, there is no reason for excluding water and ammonia in favour of carbonic acid. Moreover, it is easy to show that the carbonic acid type may be reduced to that of water. If water is the oxide of hydrogen, carbonic acid gas is the oxide of carbonyl, that is to say, the oxide of the radical carbonic oxide.

Oxides, presenting a similar constitution, may therefore be referred indifferently to one or another of these bodies. It must, however, be added, that it is more convenient to compare them with water, because, as this latter body contains two atoms of hydrogen, each of these atoms may be replaced by another

simple body, or by a radical. The number of elements and radicals being very considerable, the cases of substitution may be varied almost to infinity. There exists, therefore, an immense number of compounds which may be compared with water, if we admit that the hydrogen in this body may be wholly or partially replaced.

But does this hypothesis of elements or radicals substituted in so large a number of cases for the hydrogen of water rest upon a solid base? Is it founded upon facts, or is it merely a vain supposition? It is time to answer this question.

Let a piece of potassium be thrown upon water: it will decompose the water with such violence that the evolved hydrogen will be set on fire by contact with the globule of metal. In the molecule of water decomposed, the hydrogen will be replaced by potassium, and caustic potash will be formed. It is this fact which the theory of types expresses, by saying that hydrate of potassium is water in which an atom of hydrogen has been replaced by an atom of potassium.

Now let us take the organic chloride which Gerhardt obtained by distilling acetate of soda with perchloride of phosphorus, namely the chloride of acetyl. This body placed in contact with water, decomposes it immediately, its chlorine taking hold of an atom of hydrogen forms hydrochloric acid, and the radical acetyl just separated from the chlorine takes

the place of this atom of hydrogen just separated from the water. Acetic acid is thus formed by an interchange of elements between chloride of acetyl and water; the water is therefore actually transformed into acetic acid by substitution of the radical acetyl for an atom of hydrogen. The theory of types exactly expresses this fact, in attributing to acetic acid, that is to say, to hydrate of acetyl, a formula of extreme simplicity, and formed, as it were, on the model of that of water.*

This formula expresses nothing more than the reaction just considered; it represents one of the modes of formation of acetic acid; it supposes this acid to contain a radical capable of passing undecomposed from one combination to another by way of double decomposition; it reminds us, in the simplest manner, of the relations existing between acetic acid, chloride of acetyl, aldehyde or hydride of acetyl, acetone or methylide of acetyl, acetamide, acetic anhydride, and, in general, all the compounds which contain the radical acetyl. Here is a numerous relationship, a large family, all whose members exhibit a certain degree of resemblance, and possess a common base, namely, the oxygenated radical of acetic acid.

It is the same with all typic formulæ. Founded on the attentive study of reactions, they reflect faith-

* Note 11, p. 203.

fully the image of those reactions, and represent clearly the relations of derivation which they create between bodies. And these reactions are generally double decompositions, which do not compromise the existence of the radicals, these latter remaining unaltered, and being carried, by way of exchange, from one compound to another. Nothing can be simpler, nothing can be clearer, than the representation of these metamorphoses in the typical notation. This, indeed, was the chief advantage of the beautiful conception of types. To mark their true character, Gerhardt called them types of double decomposition.

Typical formulæ, therefore, express reactions, and it is from the facts themselves that the idea of types derives its origin, and its mode of being. Do we then mean to say that this theory can give an account of all facts, and that its typical symbols and equations are adapted to the expression of all possible reactions? It could not be so. Among the large number of metamorphoses which organic bases are capable of undergoing, the theory of types had limited itself to selecting the most simple; those, namely, which, while they modify the external form of the chemical molecule, and the nature of its appendages, do not touch the body of the substance, that is to say, its compound radical. But there are reactions in which this radical itself is modified or decomposed; in which, indeed, instead of passing unchanged into another

compound, it gives way. These deep metamorphoses do not for the most part consist of double decompositions, and cannot be represented by the comparatively simple formulæ which express the latter.

Thus, having traced the theory of types in its origin and its developments, we have at length arrived at its limits. It had taken from the radical theory the idea of those groups of atoms which act like simple bodies; but instead of representing them as bodies possessing a real existence, and the force of combination which characterises the elements, it regarded them as residues, capable of being substituted for simple bodies, and thus forming a great number of combinations belonging to a small number of types. Berzelius had imagined a host of radicals, saying: 'they will be isolated some day.' Gerhardt said: 'they are residues of molecules which cannot exist in the free state, but, nevertheless, can be substituted for simple bodies in the compounds in which they exist.' It was thus that the theory of types appropriated to itself the idea of radicals, regenerating it by the idea of substitution. By adapting these two notions to theories hostile till then, it put an end to the opposition.

But though it admitted radicals, it did not seek to penetrate their constitution. It represents them in any single formula as groups of atoms intimately united together; it exhibits their evolutions when they pass from one compound to another; but when

they are themselves decomposed, it is for the most part powerless to depict this deep transformation which reaches the very substance of the organic molecule, for it takes no account of the manner in which the radicals are made up.

A theory is good when it succeeds in grouping facts together in logical order; it is fertile when it gives rise to discoveries, and bears within itself the germ of important advances. Neither of these advantages has been wanting to the theory of types. From its latest developments there has sprung a new conception more general and capable of supplying the deficiency just pointed out. We speak of the theory of atomicity. This, however, is not the place to explain it, and we must confine ourselves to indicating that it has its roots in the theory of types. The latter, by a final evolution, had established condensed and mixed types. Williamson had referred sulphuric acid to two molecules of water in which two atoms of hydrogen are replaced by the bibasic radical sulphuryl. This radical being able to substitute itself for two atoms of hydrogen taken from two molecules of water, joins together the residues of these molecules, and rivets them together into a single *condensed** molecule. Such is the origin of the doctrine of polyatomic radicals, to which Gerhardt, following Williamson's example, referred

* Note 14, p. 206.

the acids analogous to sulphuric acid, and capable, like it, of saturating several molecules of base.

These polyatomic radicals play a similar part in mixed types. Consider a molecule of water placed side by side with a molecule of hydrochloric acid. You may imagine the atom of hydrogen of the latter, as well as one hydrogen atom of the neighbouring molecule of water, to be replaced by a bibasic radical, sulphuryl for example. This radical will then join the molecule of water which has lost an atom of hydrogen to the molecule of hydrochloric acid, which has likewise lost its hydrogen, and thus these two molecules will be riveted together by means of this bibasic radical. This is what Dr. Odling calls a *mixed type*.*

Such are the last developments of the theory of types. They mark the origin of a new period into which the science is about to enter, and is at this moment actually going through. We shall, therefore, have occasion to return to them in explaining the theories of the present day.

Gerhardt, though he had the satisfaction of witnessing the triumph of most of his ideas, did not live to see the fruitful transformation which they have undergone in these latter years. He died at the age of forty, soon following to the grave his friend and predecessor, Laurent.

* Note 14, p. 206.

Both died young, exhausted by a vast amount of work, and without having gained that popular favour which leads to honours. They did not seek it. Loving science for its own sake, they approached her by paths inaccessible to the greater number. Independent in spirit, they shook off the dust of the schools; ardent of heart, they did not shun the strife, meeting rather with opposition than with serious refutation, and resisting with firmness the most powerful of their opponents, Berzelius. In spite of the insufficiency of some of their ideas, and of certain exaggerations of language, they came out victorious from these discussions, bequeathing to their successors a great example, and to history two inseparable names.

THEORIES OF THE PRESENT DAY.

The theory of types embraced an immense number of compounds, both mineral and organic, which it classified by comparing them with a small number of very simple combinations. It overthrew the barriers which custom had raised up between mineral and organic chemistry; it classified and compared a multitude of bodies of very various nature, without distinction of origin. Giving up the idea of discovering the constitution of bodies, it grouped them according to their metamorphoses. It created a notation which was incomparable for clearness of expression, and has been the instrument of numerous discoveries, by enabling us to seize, at the first glance, on analogies or bonds of relationship. In a word, it possessed all the characters and all the advantages of a good theory. But it did not go to the root of things, and even its principle seemed to have somewhat of an artificial character. It admitted typical combinations without explaining their mode of existence. What did the types hydrogen, water, and ammonia represent?

and what reason was there for choosing these rather than others? This is an important question, which was not mooted, in the first instance, by the theory of types, but which is now resolved. These types represent various forms of combination which are related to a fundamental property of atoms called atomicity. This is a new idea which now forms the very basis of the science. We proceed to explain its origin and progress.

I.

Berzelius, in his memorable researches on the composition of salts, was led to confirm and define an important proposition, first enunciated by Richter, namely, that the capacity of saturation of an oxide depends on the quantity of oxygen which it contains. There exists in all neutral salts a constant ratio between the quantity of oxygen in the oxide and the quantity of oxygen in the acid. Such is the formula of Berzelius.

This proposition, first enunciated in 1811, gave a new point of support to the atomic theory, which was then beginning to gain ground. It may indeed be said to be a consequence of that theory. In fact, since the combination of an oxide with an acid always takes place according to the same proportions, and since the smallest quantities of the oxide and acid

that can unite together contain a determinate number of oxygen atoms, it is clear that the ratio between the oxygen of the oxide and that of the acid must be invariable.

The smallest quantity of calcium oxide that can exist contains 1 atom of oxygen; the smallest quantity of anhydrous sulphuric acid that can be conceived contains 3 atoms of oxygen. This is what was then called an equivalent of that oxide and that acid. It is these equivalents which combine together. Calcium sulphate contains, therefore, one equivalent of sulphuric acid and one equivalent of calcium oxide, and all sulphates whose oxides, like lime, contain one atom of oxygen, have a similar constitution.

Now, Berzelius first perceived that aluminium oxide, or alumina, the earth which exists in clay, and may be extracted from alum, contains 3 atoms of oxygen to 2 atoms of metal.* Applying to sulphate of alumina the law of composition which he had discovered for the sulphates, he concluded that this salt contains 3 equivalents of sulphuric acid to 1 equivalent of alumina. In fact, in order that the ratio of 1 to 3 may be preserved in such a sulphate, the oxide, which contains 3 atoms of oxygen, must find 9 in the acid: it must, therefore, take up 3 equivalents of sulphuric acid. Ferric, chromic, and manganic oxides have a composition analogous to that of aluminium

* Note 15, p. 206.

oxide, and combine, in like manner, with three equivalents of sulphuric acid.

The composition of the various sulphates indicates, therefore, a fundamental difference in the properties of the two classes of oxides, of which lime and alumina are the representatives.

Whilst 1 molecule of the former combines with only 1 molecule of sulphuric acid, 1 molecule of the latter unites with 3 molecules of the same acid. And yet, by a singular confusion of ideas, the molecule of lime was regarded as *equivalent* to the molecule of alumina, although the latter was known to combine with a quantity of sulphuric acid three times as large. This inconsistency did not escape the acute mind of Gay-Lussac; and those who attended the lectures at the École Polytechnique forty years ago, may remember that he noticed and corrected it. To bring the formula of sulphate of alumina into accordance with that of sulphate of lime, he divided the molecule of alumina into three parts, supposing it to contain an atom of oxygen and $\frac{2}{3}$ of an atom of aluminium, this proportion of oxide being joined in the sulphate to a single molecule of sulphuric acid. By this proportion of oxide, he indicated the true equivalent of alumina compared with lime: for it is clear that only those quantities of oxide can be regarded as equivalent which unite with equal quantities of acid.

But Gay-Lussac's formulæ were not received; and

chemists have maintained, instinctively as it were, those of Berzelius, which, in fact, expressed the true molecular magnitudes, and marked a decided difference in the combining capacities of two classes of oxides, the one mono-acid, and the other tri-acid, if we may so express it.

A difference of the same order was subsequently pointed out for acids. Everybody is familiar with the beautiful discoveries of Graham, who introduced into chemistry the notion of polybasic acids, parallel, to a certain extent, to that of the polyacid bases just mentioned.

Chemists had been struck with certain differences of character presented by phosphoric acid in solution, accordingly as this solution has been recently prepared with the anhydrous or the vitreous acid, or has been kept for some time. Berzelius, supposing that the compound of oxygen and phosphorus existing in these solutions is always the same, sought for the cause of these differences in a peculiar state of the substance, that is to say, in a variable arrangement of the atoms. He was the first to suppose that bodies which exhibit the same composition may have different properties, if the same elements are combined in them in different ways. It was these facts and others, which need not here be mentioned, that introduced into the science that notion of isomerism which at present holds in it so important a place, and

has so much exercised the sagacity of chemists. But it has happened, by a singular coincidence, that the different phosphoric acids do not belong to the class of isomeric bodies: they do not indeed exhibit the same composition. Doubtless they all contain that compound of oxygen and phosphorus which Berzelius supposed to exist in them. But this oxygenated body, this anhydrous acid, is united therein with different proportions of water. Graham, in his classical memoir, has pointed out the existence of three compounds of water and anhydrous phosphoric acid. For 1 molecule of this anhydrous acid, the first of these hydrates contains 1 equivalent of water, the second 2 equivalents, the third 3 equivalents.* These are the true phosphoric acids, and it will be seen that they differ in composition. Graham, therefore, designated them by different names, which they have retained, and nobody at the present day thinks of regarding them as isomeric.

Their salts are analogous in composition to the acids themselves. The monohydrated acid takes up 1 equivalent of oxide, the trihydrated acid takes up 3 equivalents. The former gives with nitrate of silver a white, the latter a yellow precipitate. These differences, which had struck the first observers, exhibit nothing abnormal, for they are due to differences of composition. The white precipitate, or

* Note 16, p. 206.

metaphosphate of silver, contains 1 atom of silver: the yellow precipitate, or ordinary phosphate of silver, contains 3 atoms. This is expressed by saying that metaphosphoric acid is monobasic: ordinary phosphoric acid, tribasic.

We have thus arrived at the point which we wish to bring to light. There are some acids whose molecule is so constituted as to require for saturation only one 'equivalent' of a certain base, whereas other acids take up two equivalents, and others again require three. Have, then, the molecules of these acids the same value? and are they equivalent among themselves? By no means, since their capacity of combination, expressed by the proportions of base which they saturate, varies as the numbers 1, 2, and 3.

Let us compare together nitric, sulphuric, and phosphoric acids. To form a perfectly saturated salt the first combines with one molecule of potash, the second with two, the third with three molecules; and if we regard as equivalent the molecules of acids which saturate the same quantity of base, we shall be obliged to admit that 1 molecule of sulphuric acid is worth two molecules of nitric acid, and that one molecule of phosphoric acid is worth three molecules of nitric acid.

Such is the important notion of polybasic acids. It exhibits the same signification and the same scope as the fact of polyacid bases, and yet for twenty years

nobody perceived any connection between the two. The two notions remained isolated in the science and lost, as it were, for theory: their connection has, however, been brought to light by recent discoveries.

That which Berzelius admitted in the case of alumina and ferric oxide, which he represented as saturating three molecules of acid, Berthelot has shown to exist in the case of glycerin, which he regards as requiring three molecules of an acid to form a perfectly saturated neutral fat. It was known before his researches that glycerin plays the part of an alcohol, that is to say, of an organic hydrate capable of forming compound ethers by combining with acids. Fifty years ago, at a time when organic chemistry was in its infancy, Chevreul, in his admirable researches on the fatty bodies, had compared the neutral proximate principles contained in oils and fats with compound ethers. This was a great and powerful idea, a ray of light in the midst of profound darkness. This idea was brought to light by careful study of the phenomena of saponification, and gave rise to the following comparison: just as compound ethers are resolved, under the influence of alkalis, into alcohols and alkaline salts, so likewise are neutral fatty bodies decomposed, under the influence of bases, into glycerin and salts called soaps. Glycerin plays, therefore, in neutral fatty bodies the same part that alcohol plays in ethers. It is an alcohol.

But, whereas common alcohol unites with only one molecule of a monobasic acid to form a compound ether, glycerin takes up as many as 3 molecules of such an acid to form a neutral fat. Thus, stearin, which enters into the composition of most animal fats, contains the elements of 3 molecules of stearic acid combined with a single molecule of glycerin, and this union is attended with the elimination of 3 molecules of water. This tristearic ether is not, however, the only compound that glycerin can form with stearic acid; instead of combining with 3 molecules of that acid, glycerin can take up only 2, with elimination of 2 molecules of water: it may also take up only 1 molecule of the acid, with elimination of one molecule of water. There exist, then, three definite compounds of stearic acid and glycerin, containing respectively 1, 2, and 3 molecules of stearic acid. All three are neutral to test-paper, but only one of them can be considered as saturated with acid, namely, that which contains 3 molecules of the acid. These facts were discovered by Berthelot, and described by him in a justly celebrated memoir, published in 1854. Their theoretical importance was not overlooked by their discoverer, who expressed himself thus: — 'These facts show us that glycerin exhibits, with regard to alcohol, exactly the same relation that phosphoric acid exhibits with regard to nitric acid. In fact, whereas nitric acid

produces only one series of neutral salts, phosphoric acid gives rise to three series of neutral salts, ordinary phosphates, pyrophosphates, and metaphosphates. These three series of salts, decomposed by strong acids in presence of water, reproduce one and the same phosphoric acid.

'In like manner, whilst alcohol produces only one series of neutral ethers, glycerin gives rise to three distinct series of neutral compounds. These three series, when completely decomposed in presence of water, reproduce one and the same body—glycerin.*

The double comparison which Berthelot here establishes between alcohol and nitric acid on the one hand, glycerin and phosphoric acid on the other, is exact only on condition that the acid compared with glycerin is tribasic phosphoric acid. To saturate it, this acid requires 3 molecules of a base like caustic potash. But it can also take up only two, or even only one: whence arise three series of phosphates with 1, 2, or 3 equivalents of base, corresponding to the three series of glyceric compounds containing 1, 2, and 3 equivalents of acid; and just as these three series of phosphates contain only a single acid—tribasic phosphoric acid—so likewise do the three series of glyceric compounds contain only a single base, namely, triatomic glycerin.

* *Annales de Chimie et de Physique*, 3ème série, xli. 319.

It was, therefore, inexact to compare the glyceric compounds containing two equivalents of acid with the pyrophosphates, and the glyceric compounds containing one equivalent of acid, with the metaphosphates. These three acids, with regard to their capacity of saturation, exhibit fundamental differences. If triatomic glycerin, as we now say, resembles tribasic phosphoric acid, it cannot be compared, with regard to its combining capacity, with bibasic pyrophosphoric or monobasic metaphosphoric acid. To compare glycerin at the same time with a tribasic, a bibasic, and a monobasic acid, would be to attribute to it at once the characters of a triatomic, a diatomic, and a monatomic alcohol. There was in this a confusion of ideas which did not exist in the facts themselves: for Berthelot's experiments were exact, and they mark a very important step—the discovery of polyatomic alcohols.

The true interpretation of all these facts was given some months afterwards by Wurtz, in a note entitled *Théorie des combinaisons glycériques*. Glycerin is there represented as a *tribasic alcohol* containing 3 equivalents of hydrogen replaceable by 3 groups or compound radicals. The three series of glyceric compounds obtained by Berthelot are regarded as derived from this tribasic alcohol by the substitution of 1, 2, or 3 radicals, for 1, 2, or 3 atoms of hydrogen. Thus tristearin appears as glycerin in which

three atoms of hydrogen have been replaced by three radicals of stearic acid (stearyl).

It would be unnecessary to mention this interpretation of the formula of glycerin proposed on this occasion, had it not given rise to an important development of the theory of radicals. This we proceed to explain.

II.

The theory of types had just been regenerated by Williamson and Gerhardt. Mineral and organic bodies were represented as derived from a small number of typical compounds by the substitution of radicals for the hydrogen of these types. Williamson was the first to point out that sulphuric acid might be represented as derived from two molecules of water by the substitution of the bibasic radical of sulphuric acid (sulphuryl) for two atoms of hydrogen. Applying this idea to glycerin, the author represented this body as derived from three molecules of water, by substitution of the tribasic radical glyceryl for three atoms of hydrogen taken from three molecules of water. But he did not stop there. Making a new step, he endeavoured to give the theoretical reason of this remarkable property of the radical of glycerin to lay hold, as it were, of 3 molecules of water, by substituting itself for an atom of hydrogen in each of them. He remarked that the radical

glyceryl, formed of 3 atoms of carbon and 5 atoms of hydrogen, contains 2 atoms of hydrogen less than the radical propyl, which can take the place of only 1 atom of hydrogen. In fact, in propylic alcohol the propyl occupies the place of 1 atom of hydrogen belonging to 1 molecule of water. The loss of 2 atoms of hydrogen, which has transformed the propyl into glyceryl, has, therefore, augmented by two units the capacity of substitution of former radical; in other words, the monobasic radical has become tribasic by giving up 2 atoms of hydrogen. This point of view was new, and has led to important consequences relating to the saturating capacity of radicals: their capacity of saturation, which has been called *atomicity*, was thereby connected with their composition itself. It depends on the number of hydrogen atoms which they contain and increases by unity for each of those atoms removed from a hydrocarbon. These ideas soon received an experimental confirmation, which has contributed to diffuse them.

To form a neutral ether, alcohol takes up only one molecule of a monobasic acid; glycerin may take up as many as three molecules. There should therefore exist bodies intermediate between alcohol and glycerin capable of etherifying two molecules of an acid. Such is the reasoning which led to the discovery of the glycols or diatomic alcohols. There was no known body which exhibited the properties of this class of

alcohols, and after their existence had been theoretically conceived, it became necessary to think of the means of creating them. This end was attained by the considerations above developed, respecting the functions of the radical glyceryl.

Diatomic alcohols might be expected to contain a diatomic radical, and olefiant gas, or ethylene seemed to fulfil the conditions of such a radical. It contains, in fact, one atom of hydrogen less than the monatomic radical ethyl. It must, therefore, be diatomic. In fact, it unites with two atoms of chlorine to form dichloride of ethylene or olefiant gas. If, then, to the chloride of ethyl or hydrochloric ether there corresponds a hydrate of ethyl, which is alcohol, there should also be a dihydrate of ethylene corresponding to the dichloride of ethylene. Wurtz effected the formation of this body by causing the di-iodide or dibromide of ethylene to act on two molecules of silver acetate, and decomposing by potash the diacetate of ethylene which is produced by this double decomposition, together with bromide of silver.

The synthetic process just indicated presents the character of a general method, and has been applied without difficulty to the preparation of bodies analogous to glycol in their composition and properties. The author has named them *glycols*, characterising them as diatomic alcohols,* to indicate their com-

* Note 17, p. 206.

bining power, which is double that of common alcohol, and is moreover in proportion to the greater complexity of their molecule.

At the time of which we are speaking, the theory of types reigned supreme in chemical science. We have already observed how the author was led by it to give the true interpretation of the facts concerning glycerin. The same theory was also the clue which led him to realise the discovery of glycol.

This body was referred, like all its analogues, to the water type, but to a condensed type formed of two molecules. The radical ethylene, which combines with two atoms of chlorine and bromine, may also be substituted for two atoms of hydrogen taken from two molecules of water, which it rivets together, because it is itself indivisible. Such is the idea enunciated by the author respecting the function of the radical ethylene in glycol, and expressed by the typic rational formula which he assigned to that body.*

Here, however, follows an important development. To the glycols thus constituted the author has been able to refer, not only the neutral compounds which they form with acids, and in which their diatomic radical remains intact, but likewise the acids which result from their oxidation, and in which their diatomic radical is modified by substitution.

Alcohol, when oxidised under the influence of

* Note 18, p. 207.

platinum black, exchanges two atoms of hydrogen for one atom of oxygen, and becomes acetic acid. The radical is modified by substitution and converted into acetyl.

Under the same circumstances, and by a perfectly similar reaction, glycol is converted into glycollic acid; but whereas alcohol by oxidising forms only one acid, glycol can form two. Under the influence of powerful oxidising agents, it exchanges 4 atoms of hydrogen for 2 atoms of oxygen, and is converted into oxalic acid. Two acids are therefore derived by oxidation from glycol, the radical of which can be twice modified by substitution, exchanging 2 or 4 atoms of hydrogen for 1 or 2 atoms of oxygen. This substitution takes place in the radical ethylene, which becomes successively the radical glycollyl in glycollic acid, and the radical oxalyl in oxalic acid. Both these acids are diatomic, for they belong to a diatomic alcohol; but, whereas one of them, namely, oxalic acid, is bibasic, the other, glycollic acid, is only monobasic.* The author, to whom the discoveries of these reactions is due, was the first to remark that the basicity of acids increases with the number of oxygen atoms contained in their radical, and that the terms polyatomic and polybasic are not rigorously synonymous, when applied to acids. He immediately extended these reactions to the other

* Note 19, p. 208.

glycols, the higher homologues of ordinary glycol, which he had obtained by means of hydrocarbons, the higher homologues of ethylene, and amongst which he had particularly studied propyl-glycol and amyl-glycol. The former by oxidation yielded lactic acid, the second a new acid of the lactic series.

It was thus that the polyatomic and polybasic acids were connected with the polyatomic alcohols, just as the monobasic acids, analogous to acetic acid, had previously been connected with the monatomic alcohols.

In connection with the classification of organic substances, these facts appear highly important; it may indeed be maintained with good reason that they have been the occasion and the origin of a new mode of exposition in organic chemistry. They have, in fact, afforded the means of forming into a separate group the polyatomic alcohols, with the whole train of compounds belonging to them, such as the hydrocarbons which form their radicals, and the polyatomic acids resulting from their oxidation, with which also may be joined the aldehydes. All these bodies may be grouped together under the name of *polyatomic compounds*, and definitively separated from the monatomic alcohols and acids, and all the bodies thereunto related. We see, then, that the alcohols of different atomicity have become to a certain extent the base of the classification, and this

base has been greatly enlarged by the beautiful experiments of Berthelot on mannite and the saccharine substances. These bodies have been characterised as hexatomic alcohols. They require for saturation six molecules of a monobasic acid, whereas glycerin requires only three, glycol takes only two, and common alcohol is contented with one.

To appreciate the value of this service rendered to classification, it is sufficient to remember the mode of exposition adopted in courses of organic chemistry twenty years ago. After a few preliminary remarks on the composition and analysis of organic substances, it was usual to commence with the neutral proximate principles furnished by the vegetable kingdom, such as cellulose, starch, and saccharine substances. With these, also, were often connected the neutral substances of the animal organism, namely, albumin and its congeners. Thus the course was begun with the most complex substances, the constitution of which was absolutely unknown; and these were followed by the simpler substances resulting from their decomposition, the order of this exposition being determined solely by the fortuitous coincidence of certain general properties, such as neutrality, acidity, and alkalinity—never by the consideration of bonds of relationship or derivation. All the acids were grouped together by the single circumstance that they redden tincture of

litmus; all the alkalis were grouped together because they change it back again to blue. This was the infancy of the art. At the present day, bodies are grouped according to the increasing order of their molecular complication, beginning with the simplest, and rising progressively in the series in proportion as the molecules become more complex.

But, what! Is this complication of the molecule to be determined strictly and solely by the number of carbon atoms that it contains? and are we to recur for a principle of classification to Gerhardt's scale of combustion (p. 108)? By no means. A new element enters into the considerations by which the molecular complication is determined, namely, the atomicity or combining capacity of the molecule, which may be expressed by referring the molecule to a type more or less complex in proportion to the atomicity or saturation of the radical contained in that molecule. From this point of view, oxalic acid, though it contains only 2 atoms of carbon, belongs to a higher type of combination than stearic acid, which contains 18 carbon atoms. The former is diatomic, and is related to a diatomic alcohol; the latter is monatomic, and related to a monatomic alcohol. It follows, therefore, that the principle of classification now generally adopted is derived from atomicity. Bodies of equal atomicity are placed together as forming great classes. The properties of all these

bodies differ from one another according to the nature, number, and arrangement of the elements which they contain. Hence the facility of establishing subdivisions in these great classes, and of grouping bodies of the same class by series and by families.

The *series* includes those which, possessing similar molecular structure and analogous properties, exhibit regular variations in their composition, so that the difference observed between two neighbouring molecules is reproduced in like manner for all the others. All bodies of the same series belong to the same type.

The *family* comprises all bodies having in their composition a common element, which is the radical; this may enter into the most various combinations. Hence result compounds belonging to different types and possessing dissimilar properties, although they all contain the same nucleus.

In the series of alcohol are placed all those bodies which exhibit with alcohol certain relations of composition and properties.

In the family of alcohol are grouped all bodies containing the same radical, namely, ethyl.

Such are, in a few words, the principles of classification now adopted in organic chemistry. It will be seen that atomicity, that is to say, the combining capacity of bodies, enters in these considerations as a dominant element. It is proportional, as above stated, to the atomicity of the radicals which the

compounds contain. It remains to explain the ideas which have been started concerning the mode of generation of these radicals.

The discovery of the polybasic acids had pointed out differences in the saturating capacity of acids; that of the polyatomic alcohols had indicated differences of the same order in the combining capacity of alcohols. It is doubtful whether any general notion could have been deduced from these facts, had not the theory of types sought to refer the observed variations in the combining capacities of acids and alcohols to corresponding differences in the saturation of the radicals which they contain.

It was said: Triatomic glycerin contains a radical which is triatomic, because it wants three atoms of hydrogen to bring it to the state of saturation. Diatomic glycol contains a radical which is diatomic, because it requires two atoms of hydrogen to bring it to a state of saturation.

The atomicity of radicals containing hydrogen and carbon was thus related to their richness in hydrogen, to their state of saturation so far as regards that element. This proposition, enunciated for the first time by the author in the note cited on page 142, has been developed by various chemists. We must here explain it with a few details.

One atom of carbon in marsh gas, or protocarburetted hydrogen, is combined with 4 atoms of

hydrogen, and no one has yet succeeded in obtaining a compound of carbon and hydrogen richer in hydrogen than this. Marsh gas is, however, not the only compound of its kind. It is the first term of a series of hydrocarbons, which are all saturated with hydrogen, and exhibit in their composition a regular progression of carbon and hydrogen atoms, so that each one differs from its neighbour by 1 atom of carbon and 2 atoms of hydrogen.

This is what is called the *homologous series* of marsh gas. Amongst all the hydrocarbons, the compounds belonging to this series are the richest in hydrogen. They are saturated with it, and incapable of taking up any more. But what is more remarkable, they are just as incapable of directly taking up any other element as of taking up hydrogen; and in order that another simple body, such as chlorine, may be able to find a place in their molecules, it must begin by expelling the hydrogen. In a word, these saturated hydrocarbons appear to be incapable of entering directly into combination—they can only be modified by substitution. It appears as if all the affinities residing in the carbon were satisfied by those which reside in the hydrogen atoms, the whole forming as it were a neutral system. A body thus constituted is called a *saturated hydrocarbon.*

Now, suppose such a hydrocarbon to be deprived of one atom of hydrogen; the affinities residing in the

carbon atoms will no longer be satisfied, and consequently the residue or incomplete molecule, differing from the saturated compound by one atom of hydrogen, will exhibit precisely the combining capacity which resides in this atom of hydrogen. This residue is capable of combining with one atom of chlorine, or of replacing one atom of hydrogen; in a word, it plays the part of a monatomic radical.

Now let two atoms of hydrogen be removed from a saturated hydrocarbon: the remainder of the molecule will tend to regain the affinities which resided in these two atoms of hydrogen. The incomplete molecule will be able to take up two atoms of hydrogen or two atoms of chlorine; or, again, to take the place of two atoms of hydrogen or of chlorine. These are the attributes of a diatomic radical. Lastly, the subtraction of three atoms of hydrogen from a saturated hydrocarbon will convert this compound into a triatomic radical, and so on.

These principles being established, so far as regards the generation of hydrocarbon radicals derived from saturated hydrocarbons, it became easy to apply them to all compound radicals, whatever might be their nature. In fact, any radical whatever may always be connected with a saturated compound, from which it is derived by the loss of one or of several elements, and the degree of its atomicity is marked precisely by the amount of this loss, which corresponds to a

greater or lesser number of hydrogen atoms. It is thus that the atomicity of radicals has been referred to their state of saturation: an important step, since it has established a relation between the functions of radicals and their composition. To extend this notion of saturation to the elements themselves required but one step more.

We see, then, that in historic order the notion of atomicity has been introduced into the science by degrees, and in three steps, so to speak.

First, polyatomic compounds were discovered.

Secondly, their polyatomicity was referred to the state of saturation of their radicals.

Thirdly, the notion of saturation, which was first applied to the radicals, and from which their atomicity follows, as a necessary consequence, was extended to the elements themselves.

In fact, just as compound radicals differ from one another by their capacity of saturation, so likewise do the atoms of elementary bodies exhibit differences as regards their combining capacity. There are degrees in this fundamental property of the atoms, and these degrees are marked by the atomicity. One metal is incapable of uniting with more than one atom of chlorine; another takes up two; a third combines with three atoms of chlorine; a fourth requires four atoms to form a saturated chloride. Such inequalities in the combining capacities of the

metals for chlorine are inherent in the nature of their atoms, and it is for this reason that they are designated by the name of atomicity.

This theoretical notion now governs the whole science, and it is important to inquire carefully into its origin and to trace its development.

III.

Let us return for an instant to the theory of types. Laurent having compared metallic protoxides and their hydrates with water, Dr. Odling pointed out that the trioxides and their hydrates may be derived from several molecules of water. Remembering that hydrated sulphuric acid had been regarded as derived from two molecules of water by the substitution of the radical sulphuryl for two atoms of hydrogen, the learned and ingenious friend of Dr. Williamson showed that hydrate of bismuth may be derived from three molecules of water by substitution of the metal bismuth for three atoms of hydrogen; and this value of substitution, or combination, was indicated by three dashes placed above the symbol. This notation, introduced by Odling, has stood its ground, and the principle which it laid down, the non-equivalence of the atoms of elementary bodies, has since been generalised.

Atoms are not equivalent, but exhibit among themselves differences of the same order as mono-

basic, bibasic, and tribasic acids. In a memoir published in 1855 the author characterised nitrogen and phosphorus as tribasic elements.* He even endeavoured to account for this capacity of combination by supposing that each atom of these elements was formed of three sub-atoms indissolubly united together, and each capable of replacing one atom of hydrogen. This substitution taking place in three molecules of water, the atom of phosphorus thus formed a link between these three molecules of water, which it riveted together in such a manner as to form phosphorous acid. Thus, not only was the atomicity of phosphorus and nitrogen clearly pointed out, but an attempt was even made to account for it by a hypothesis which has since been reproduced.

Such was the origin of the theory of the atomicity of elements. In 1858 this theory made a decided step forward.

Kekulé, in an important memoir upon radicals,† broached the idea that carbon is a tetratomic radical; he was led to it by the consideration that in the simplest organic compounds, one atom of carbon is always united with a sum of elements equivalent to four atoms of hydrogen. It is thus in marsh gas, in perchloride of carbon, and in all the intermediate compounds containing both hydrogen and chlorine.

* *Annales de Chimie et de Physique*, 3ème série, xliv. 306.

† *Annalen der Chemie und Pharmacie*, cvi. 129 (1858).

These two elements are equivalent, since they replace one another atom for atom. In the compounds in question their sum is always equal to four. Similarly, in carbonic acid, the two atoms of oxygen combined with a single atom of carbon are equivalent to four atoms of hydrogen; for each of them has the power of uniting with or replacing two atoms of hydrogen. But, it will be said, one atom of carbon can content itself with a single atom of oxygen, as indeed it does in carbonic oxide. It is true, indeed, that this body contains only a single atom of oxygen, but then it is not saturated. The affinity which resides in the atom of carbon is not satisfied by its union with the single atom of oxygen. This is why carbonic oxide can unite directly, either with a second atom of oxygen, when it is transformed into carbonic acid, or with two atoms of chlorine, whereby it is converted into phosgene gas.

In both these compounds the carbon has exhausted its affinity in taking up a sum of elements equivalent to four atoms of hydrogen. By being saturated, it has become tetratomic. It is thus that the notion of saturation enters into the determination of atomicity. It has likewise entered into another consideration developed by Kekulé in the memoir above cited.

In the series of saturated hydrocarbons, the number of hydrogen atoms is equal to four times the number of the carbon atoms, only in the first term, or

marsh gas, which contains but one atom of carbon. How does it happen that in the following term two carbon atoms are united with only six atoms of hydrogen, instead of eight? Kekulé accounts for this fact by supposing that each of the two carbon atoms loses one atomicity in soldering itself to the other, or rather in combining. Having thus exchanged two atomicities, these carbon atoms keep only six of the eight which they formerly contained, and can now fix only six atoms of hydrogen. It is the same with the other terms of this series, which contain 3, 4, 5 atoms of carbon. These latter are soldered together, thus forming a chain, the links of which are riveted by a part of the force of combination. Another portion remains to a certain extent disposible, and serves to attract and fix other elements which group themselves round the atoms of carbon. These constitute the nucleus of the combination—its solid framework; the atoms of hydrogen, chlorine, oxygen, &c., which attach themselves to it, form its appendages.*

This is a great idea, for it explains the fact of the complication of organic molecules, and serves to account for their structure.† Why, indeed, do the

* See the end of note 20.

† It should not be forgotten that Couper has developed analogous ideas without previous knowledge of the propositions enunciated by Kekulé, which have exerted so great an influence on the latest development of organic chemistry.

atoms of carbon exhibit this singular tendency to accumulate in large numbers in organic molecules? Because they possess the property of combining together, of riveting themselves one to the other. This important property gives to the innumerable compounds of carbon a peculiar stamp, and to organic chemistry its physiognomy, its mode of being. No other element possesses this power in the same degree. Doubtless hydrogen can combine with itself, as recognised by Gerhardt: but, as an atom of this body exhausts its combining capacity by its union with a second atom, no other element can be added to this couple, the saturated molecule of which is reduced, as it were, to its simplest expression, being formed of two atoms.

The polyatomic elements alone, after having expended part of the combining capacity which resides in them, in riveting themselves one to the other, can retain another part to fix other elements. This power is possessed by the atoms of carbon, and likewise by the atoms of oxygen. The latter are diatomic, and can exchange their atomicity two by two. It is supposed that this is the case in free oxygen, which is formed of two atoms, occupying two volumes, if one atom of hydrogen occupies one volume. These two atoms possessing four atomicities, have exchanged them by fixing themselves one upon the other. But if each of them can lose two atomicities,

by a complete exchange, they can also, by a simple exchange, lose only one, each retaining an atomicity disposible, as it were, and serving to fix an atom of hydrogen or of chlorine.

Suppose two atoms of hydrogen to fix themselves in this manner on a couple of oxygen atoms united by the exchange of a single atomicity: the result of this combination will be the peroxide of hydrogen, formed of two atoms of oxygen and two atoms of hydrogen. The fixation of two chlorine atoms on this couple of oxygen atoms will give rise to the peroxide of chlorine; that of one hydrogen atom and one chlorine atom, to chlorous acid.*

From the considerations just developed, it is easy to deduce the molecular structure of the oxygenated compounds in question. It is evident that the oxygen atoms in hydrogen peroxide or chlorine peroxide, being riveted one to the other, each of them is united with one atom of hydrogen or of chlorine. Such are the relations existing between the atoms in these comparatively simple compounds. These relations mark the structure of the molecule. They are discovered by induction, based upon the double notion that the atoms of oxygen are diatomic, and that they are capable of soldering themselves together.

Facts and arguments of the same kind may be

* Note 20, p, 208.

invoked when we have to determine the grouping of the atoms in more complex compounds, especially in the compounds of carbon, that is to say, organic compounds.

The ordinary elements of these compounds are carbon, hydrogen, oxygen, and nitrogen. The tetratomic carbon atoms being soldered together, and forming, as above mentioned, the nucleus of the combination, the other elements of various atomicity group themselves around the former, saturating, by their atomicities, those which have remained free in the chain of carbon atoms. Now, in a system of this kind, the grouping of the atoms is often necessarily determined by their number and their nature. In fact, in organic compounds said to be saturated, all the atomicities are satisfied, and this they can be only on condition that the atoms are grouped in a certain manner. Let us take an example to define the sense of this proposition, and show its importance.

We are acquainted with a gas formed of 2 atoms of carbon and 6 atoms of hydrogen. It belongs to the series of hydrocarbons, the richest in hydrogen of any that are known. In this compound the 2 carbon atoms are soldered together, and, in thus uniting, each of them has exchanged and lost one atomicity. Each, therefore, retains 3 atomicities, and fixes 3 atoms of hydrogen. Here, then, is

a very simple system, in which the 6 atoms of hydrogen are grouped symmetrically round the 2 atoms of carbon. This is the gas called hydride of ethyl. The compound is saturated, for all the atomicities are satisfied. It cannot, therefore, attach to itself any other atoms, but can only be modified by substitution. Thus, it can give up an atom of hydrogen and take another atom in its place. Suppose an atom of chlorine to present itself in this manner: there will be formed a chlorinated compound, the chloride of ethyl, which is saturated, like the hydrogen compound from which it is derived: for the atom of chlorine which has entered it, is of the same value as the atom of hydrogen which has gone out.*

Suppose one hydrogen atom of the ethyl hydride to be expelled by an oxygen atom: it is clear that the latter will fix itself by one of its atomicities on the carbon atom, to which was attached the atom of hydrogen which it replaces; but, being possessed of two atomicities, it retains one of them, which is disposible. It tends, therefore, to saturate itself by fixing another atom, an atom of hydrogen, for example, which it draws, as it were, into the combination. The result is, therefore, the same as if a hydrogen atom of the ethyl hydride were replaced by a group formed of one atom of oxygen and one atom of

* Note 21, p. 209.

hydrogen; and this group, now called *orhydryl*, or *hydroxyl*, is nothing else than water which has lost an atom of hydrogen. Such a residue is monatomic, and can take the place of an atom of hydrogen.

It is thus that ethyl hydride is converted into ethyl hydrate, which is alcohol. The part here played by the oxygen is easily understood: it is attached by one of its atomicities to a certain atom of carbon, by the other to an atom of hydrogen, which it joins to the ethylated molecule. The latter is the nucleus; the atom of hydrogen drawn into it is the annex; the atom of diatomic oxygen is the medium, attached on one side to the nucleus, on the other to the annex.* Such is the function of oxygen in the molecule of alcohol, and such is the distribution of the atoms in this somewhat complex molecule.

By similar reasonings we may discover the relations between the atoms in more complex derivatives related to hydride of ethyl. Suppose an atom of hydrogen in this compound to be replaced by an atom of nitrogen: the latter will fix itself by one of its atomicities to the atom of carbon to which this atom of hydrogen was attached. But since the atom of nitrogen possesses 3 atomicities, it tends to draw into the combination other elements which can satisfy them, 2 atoms of hydrogen, for example. Thus in the azotised compound called ethylamine,

* Note 21, p. 209.

the nitrogen has become the connecting link between the ethyl residue and the two annexed atoms of hydrogen.*

Such is in general the function of polyatomic elements in organic compounds. United, in a chain of carbon atoms, to one of them, they draw in their train other elements capable of satisfying the atomicities which have remained free. It is thus that oxygen, nitrogen, and carbon itself, may serve as bonds between a residue of a molecule, such as ethyl, and the annexed atoms, or between two residues, two fragments of molecules, which they solder together; and in this manner organic molecules grow, not only by carbon soldering itself to carbon, but also by means of oxygen and nitrogen, which solder themselves together or to carbon, each of these polyatomic elements drawing in its train a series of atoms more or less considerable.

These developments may suffice to show the importance of the notion of the atomicity of elements for the solution of one of the most important questions that have occupied the attention of chemists, namely, the constitution of organic compounds.

Starting from the fact that the four elements, carbon, nitrogen, oxygen, and hydrogen, differ in their capacities of combination as the numbers 4, 3, 2, 1, we can determine, in a large number

* Note 21, p. 209.

of cases, their grouping in a given compound, if we combine these notions with those which are furnished by its reactions.

What was the method formerly adopted to fix the constitution of a compound body, and construct a rational formula adapted to express it? The method consisted in studying its metamorphoses and endeavouring to penetrate the grouping of the atoms, by the various evolutions impressed upon them by the transformations of the molecule. The task was difficult, for the means were insufficient. Is it necessary to recall the opinion of Gerhardt on this point? 'It is a vain attempt,' said he, 'to construct rational formulæ, inasmuch as each body can have as many of them as it exhibits reactions.' The statement was too absolute, and was corrected by the author himself towards the close of his short and brilliant career. Has he not constructed the most elegant of all rational formulæ, namely, the typical formulæ?

These he based on the study of metamorphoses. To this method he would now add inductions deduced from the atomicity of the elements. In short, if the study of reactions yields data for the dynamics of atoms, considerations relating to their combining capacity furnish the elements of molecular statics. Here, then, are two methods, each of which serves as the complement and verification of the other.

What can we do at the present day? and what is it that we have just been doing? Wishing to determine the relations existing between the atoms in certain ethylated compounds, we have sought out the points of attachment of the affinity for the polyatomic elements, carbon, nitrogen, oxygen. The presence of these elements in a saturated organic compound entails, in fact, certain views respecting its molecular arrangement, which are subsequently corroborated by considerations drawn from the mode of formation and the metamorphoses of that compound. The synthetic process which we have employed is applicable in a large number of cases, and leads to trustworthy results when combined with the analytical data furnished by the study of reactions. This is an important step, which follows naturally from the great idea enunciated by Kekulé and Couper.*

Considerations respecting atomicity being thus applied to the study of atomic constitution, and of the internal structure of molecules, chemists have been able in a great number of cases to attempt the explanation of phenomena which formerly defied interpretation: we allude to the numerous cases of

* Amongst the chemists who have most largely contributed to develop the principles at present invoked to determine the composition of organic compounds, it is proper to mention MM. Buttlerow and Erlenmeyer. The appropriate expression 'molecular structure' is due to Buttlerow.

isomerism. Here are two bodies exhibiting the same composition, but different properties. It was always supposed that this dissimilarity was due to differences in the arrangement of the atoms, but nothing exact was known in this respect. At present we can go further, and without endeavouring to assign to each atom its absolute position in space, we may often succeed in determining its relations to the other atoms, and consequently in discovering the structure of the molecule. Given two bodies which, though differing by their properties, contain the same atoms, and in equal number, we can, by grouping the atoms in different ways, succeed in constructing with identical materials two molecules distinct by their form; and these differences of structure account for differences of properties. Thus we no longer content ourselves with establishing the fact of isomerism; we can now discover its origin and explain it.

IV.

Let us stop here for a moment, and mark the point of view attained.

Experiment had established the fact that the molecules of bases, acids, and alcohols, are not all equivalent to one another in their combining capacities. Theory, after having sought the explanation of this fact in the state of saturation of the radicals,

has transferred this notion of saturation to the elements themselves.

The atoms of elementary bodies carry into the combinations which they enter the combining capacity which they possess in various degrees. In most cases affinity is exerted between different atoms, but it may also be manifested between atoms of the same nature. It is thus that the atoms of carbon have a certain affinity one for the other; and this property, which they also share with other elements, accounts for the complexity of organic molecules, just as the capacity of saturation of the elements accounts for the structure of the molecules. Such is the development of the theory of atomicity:—the constitution of organic compounds unveiled; isomerism interpreted in a large number of cases; a system of rational formulæ, founded both on the reactions of compounds and on a fundamental property of their atoms: these are the great results attained.

This is not all: this horizon, so vast, has yet been enlarged. The new theory, in developing itself, has cemented the alliance between organic and mineral chemistry, that alliance which had been foreseen and proclaimed by great minds, and is now firmly established by the notion of atomicity. It is time to show how this notion has penetrated into mineral chemistry.

Is this fundamental property of exhibiting a capacity of multiple combination limited to the atoms

of carbon, nitrogen, and oxygen, which constitute, together with hydrogen, the ordinary elements of organic compounds? By no means. It exists also in other atoms.

We know that those elementary bodies which are called metalloïds, to distinguish them from metals, have been grouped in families. In this attempt at classification, Dumas took account of the natural affinities revealed to us by the atomic formulæ of compounds. He united in a single family chlorine, bromine, and iodine, because they unite with hydrogen atom for atom. Another family was composed of oxygen, sulphur, selenium, and tellurium, elements each atom of which unites with 2 atoms of hydrogen. Nitrogen has become the key of a third family, including also phosphorus, arsenic, and antimony, the members of which unite with hydrogen in the proportion of 1 atom to 3; with oxygen in the proportion of 2 atoms to 1, 3, and 5 atoms of that gas. We see, then, that this attempt at classification was founded on the combining capacities of the elements. In reality, M. Dumas grouped the elements according to their atomicities.

But what! Are the metals themselves all cast in the same mould as regards their capacities of combination? Must we still admit, with Gerhardt, that they can all be substituted for hydrogen, atom for atom, and that their protoxides have the same

constitution as water, that is to say, that they all contain 2 atoms of metal to 1 atom of oxygen? Such a view is no longer admissible.

The metals differ in their capacities of combination, as much as the metalloïds themselves, and may be grouped according to their degrees of atomicity.

The alkali-metals, such as potassium and sodium, with which we may also associate silver, exhibit the same combining capacity as hydrogen itself; like the latter, they are incapable of fixing more than one atom of chlorine or bromine. An atom of oxygen is too much for them; they unite in pairs to saturate it: their protoxides and hydrates therefore resemble water, the atomic constitution of which they exhibit. These metals are monatomic.

But calcium, barium, strontium, lead, and many others, take up two atoms of chlorine to saturate themselves, and cannot be satisfied with less. They are diatomic among metals, like oxygen among metalloïds. This idea of diatomic metals was first proposed by Cannizzaro, who based it on physical data; it was maintained and propagated by the author, who endeavoured to support it by chemical arguments. Amongst these latter we may cite chiefly those which are drawn from the analogy of these metals to diatomic radicals like ethylene, the functions of the one and of the other in combinations being the same. Without dilating further upon this

subject, we may say that Cannizzaro attributed to the metals in question atomic weights double of those which had been assigned to them by Gerhardt, an innovation which has introduced important changes into the notation of the last-mentioned chemist. In fact, there has thence resulted a new system of atomic weights, which is in perfect harmony with the physical data above mentioned. These latter are deduced from the laws formerly discovered by Dulong and Petit, and by Avogadro and Ampère.

The law of Dulong and Petit may be thus enunciated :—*The atoms of all elementary bodies have the same specific heat.* This law is true only on condition that the atomic weights usually assigned to a certain number of the elements shall be doubled. We appear, indeed, to be justified in adopting these double atomic weights for the sake of bringing a certain group of the metals within the scope of so simple and general a law. It does, in fact, exhibit this character of generality : for the three or four exceptions to it that have been noticed relate to elements which exhibit peculiar phenomena of allotropy, that is to say, their particles are capable of assuming several modifications, passing through different physical states, and grouping themselves in various ways. Such is the case with carbon, boron, and silicium. Are we not justified in supposing that, in the diamond,

for example, the particles of carbon exhibit an arrangement different from that which they have in wood-charcoal? And when such a body is subjected to the action of heat, may not a movement take place in its particles, an internal work, by which heat may be evolved or absorbed? It is just this quantity of heat evolved or absorbed by internal work that accounts for the slight exceptions and inaccuracies exhibited by the law of Dulong and Petit.

We may, then, conclude that this law is characterised by great generality, and affords a satisfactory verification of atomic weights: for it is evident that of two numbers which are multiples one of the other, and equally capable of satisfying chemical data, that one is to be preferred which is in harmony with the law of the specific heats. This has actually been done in the case of the metals under consideration.

It must further be added that the atomic weights thus deduced from the law of Dulong and Petit are identical with the 'thermic equivalents' of Regnault. They are, in fact, the ponderable quantities which, in absorbing equal quantities of heat, undergo equal elevations of temperature, and are therefore equivalent with regard to thermic effect.

We have already explained the hypothesis of Avogadro and Ampère. It is founded on the relations discovered by Gay-Lussac between the densities of gases and vapours and their molecular weights. It

may be thus expressed:—If an atom of hydrogen occupies one volume, the molecules of all bodies in the state of gas occupy two volumes, and consequently the weight of these two volumes will express the weight of the molecule, referred to the weight of one volume of hydrogen taken as unity. But these relative weights are nothing else than the densities, on condition that the weight of hydrogen be taken as unity. In other words, if the densities of all gases and all vapours be referred to hydrogen, the double densities of these gases or vapours will express the weights of their molecules. Hence we have a very simple method of determining and verifying the relative weights of atoms.

Now, the system of atomic weights which tends to prevail at the present day, is in accordance with this very simple law. In particular it may be said that the double atomic weights applied to the metals according to their specific heats, may likewise be deduced from the molecular weights of their volatile compounds.

In speaking of the law of Avogadro and Ampère, it is necessary to make a restriction which leads to important consequences. We are acquainted with a certain number of bodies which seem to form exceptions to this law. Their molecules, in the state of vapour, occupy not two, but four volumes, so that for these molecules the double vapour-density would

give a weight which would be only half of the true molecular weight. Let us take an example.

Everything leads to the conclusion that a molecule of sal-ammoniac is formed of one molecule of hydrochloric acid and one molecule of ammonia gas. The two component bodies have united all their elements into a more complex molecule; and if the combination is stable, if it can remain undecomposed at the temperature at which sal-ammoniac passes into the state of vapour, the molecule of this vapour should occupy two volumes. But it really occupies four. The same is the case, not only with all compounds analogous to sal-ammoniac, but also for hydriodide of phosphoretted hydrogen, pentachloride of phosphorus, sulphuric acid, and other compounds.

Here we have a rather large number of exceptions to the law of Avogadro and Ampère. They have often even been cited as arguments tending to upset this law. And they would indeed be capable of embarrassing its advocates, if they were not susceptible of a very simple interpretation, which deprives them of all demonstrative force in the question. There is, indeed, nothing to prove that the compounds in question can really exist in the state of vapour without undergoing more or less complete decomposition; their boiling points are generally high enough to render such a supposition very probable.

To resume one of the examples above cited, let us

consider sal-ammoniac. Doubtless when the elements of this salt are brought together at ordinary temperatures, they combine, with considerable evolution of heat; under these conditions the affinity of hydrochloric acid gas for ammonia gas is considerable; but it is much less, and the gases unite but partially, and with only slight development of heat, when, as in the experiments of H. Sainte-Claire Deville, they are brought together at the high temperature at which mercury boils. At this temperature the greater portions of the gases which are brought together remain uncombined in the state of simple mixture. Now, we cannot reduce sal-ammoniac to the state of vapour and take the density of this vapour, excepting at elevated temperatures, at which the affinity of the component gases is very much weakened, and these gases, which are combined together in solid sal-ammoniac, separate from one another, each of them resuming its individual existence. Under these conditions, a molecule of sal-ammoniac, which, if it remained intact, should occupy two volumes of vapour, is wholly, or almost wholly, resolved into two other molecules which remain simply mixed, each of them occupying two volumes of vapour. It is not, therefore, the molecule of sal-ammoniac that occupies four volumes of vapour, but the products of its decomposition by heat. Everything leads to the conclusion that the molecules of

the other bodies above mentioned, as furnishing exceptions to the law of Avogadro and Ampère, undergo, when heated, decomposition analogous to that which is experienced by the molecule of sal-ammoniac. They are resolved, more or less completely, according to the temperature, into their component molecules, which then occupy a volume double of that which the more complex molecule would occupy if it remained undecomposed.

But it may be said, why do we not find the trace of this decomposition when the vapour is recondensed and the body has returned to the ordinary temperature? In the flask in which you have converted the sal-ammoniac into vapour, and in which this vapour has been decomposed, you actually, after condensation, again find unaltered sal-ammoniac. It could not be otherwise. When the temperature falls, the separated elements of the sal-ammoniac again exert their affinities, and reproduce the molecule of that salt, so that there remains no trace of the temporary decomposition which it had undergone.

One of the best arguments that can be adduced in favour of this interpretation is that which is drawn from the vapour-density of hydrobromide of amylene. This body is a liquid compound of the hydrocarbon amylene with hydrobromic acid. When raised to a temperature a little above its boiling point, it exhibits a vapour-density which may be called normal, because

it corresponds to two volumes of vapour for one molecule of the compound. At this temperature the vapour is intact; but when it is further heated, it experiences a decomposition more or less complete accordingly as the heat applied is more or less considerable. Like sal-ammoniac, it is resolved into its elements, hydrobromic acid and amylene. But this decomposition is gradual; it is completed, not at a fixed degree, but between rather wide limits of temperature, so that the vapour, unaltered at a certain degree of heat, becomes mixed at higher degrees with more and more considerable portions of its products of decomposition, until at length, at a still higher temperature, the decomposition becomes complete. At this moment the density of the vapour is reduced to half its original value. Are we then to conclude that hydrobromide of amylene exhibits two different vapour-densities? Evidently it cannot be so; and it is natural to suppose that the true vapour-density is that which has been determined at a temperature low enough to justify us in supposing that the molecule still remains undecomposed, and that, if this density decreases as the temperature rises, the alteration is due to the decomposing action exerted by heat upon the vapour.

There is then reason for believing that the other exceptions to the law of Avogadro and Ampère which have been noticed are due to similar causes, and that

this law, one of the foundations of modern chemistry, subsists in all its generality. Let us not forget that it has been verified in so large a number of cases that the contrary facts undoubtedly assume the character of exceptions, and for that very reason demand careful examination. Moreover the interpretation given to them, which is now accepted by the majority of chemists, is entirely conformable to the current ideas upon affinity. Two molecules, each capable of assuming the gaseous form, are united by affinity into a more complex molecule. It may happen that the boiling point of this molecule is so low that the heat supplied for converting it into vapour does not restore to the two primitive molecules the heat which they had lost by combining: they therefore remain combined. But can we expect that it will be always so? And cannot the affinity of two bodies one for the other be so feeble, or the compound which they form so little volatile, that the point of decomposition may be situated below the boiling point? This is just what happens in most of the cases above cited; it is certain that a large number of chemical molecules are incapable of assuming the gaseous form without undergoing decomposition more or less complete.

It is very important to study the progress of this decomposition.

The phenomenon is simple enough when the pro-

ducts once disengaged and separated one from the other can no longer unite directly so as to reconstitute, by an inverse action, the compound which has just been decomposed. Suppose that the body is solid, and that the products of its decomposition can disengage themselves freely. All the molecules which constitute the mass of the decomposing body are then subject to the same conditions during the whole course of the decomposition. They are all influenced in the same manner by the heat, and all decomposed at the same temperature as soon as the quantity of heat added to them has restored to their elements the working force which these elements had lost in combining. Under these conditions the decomposition takes place at a fixed and definite temperature.

But it is not the same when the products of decomposition, remaining mixed with the compound which has furnished them by its resolution, are capable of reuniting so as to reproduce this compound. The tendency of the latter to be decomposed under the influence of heat, or to be dissociated, according to the felicitous expression of Deville, is then counterbalanced by the contrary tendency of the liberated elements to reunite under the influence of affinity. Thus there is established a kind of mobile equilibrium between the molecules of the original compound, which remain intact, and the products of its decomposition, which tend to reunite. In proportion as

the mass of the latter increases in the mixture, the sum of the affinities likewise increases, and to counteract these increasing tendencies to 'recomposition,' it is necessary to supply the molecules still to be decomposed with increasing quantities of heat. The decomposition is, therefore, a continuous phenomenon, which, far from being completed at a fixed point, takes place between certain limits of temperature. This is what is now called 'dissociation.' Every one is acquainted with the beautiful experiments of M. Henri Sainte-Claire Deville on this subject, to which we can here only refer. We will merely remark that the facts under consideration are not isolated in chemical science, and that they are related to other manifestations of affinity, especially those inverse actions produced under the influence of masses, which were formerly studied by Berthollet.

It is affinity which comes into play in all these phenomena; and though we are ignorant of the intimate nature of this force, we are at least acquainted with its relations to heat. We know that affinity cannot be overcome without evolution of heat; that it cannot be restored without absorption of heat: there is, therefore, a correlation between these forces, and they may be measured one by the other. Chemical force is supposed to reside in the atoms of bodies. It consists perhaps in a particular movement of the atoms. On this point we have no exact knowledge;

but we know that chemical force is not destroyed when the atoms in which it resides have met together and united. By the fact of this union the affinity is extinguished; it is satisfied, at least in part; but the portion of energy thus withdrawn from the atoms is not destroyed, for it reappears as heat at the very moment of combination; and the intensity of the heat evolved measures the energy of the affinity.

Is there, however, nothing in this force but the energy with which it acts? Is it uniformly exerted on all atoms with the sole difference of its intensity, just as gravity attracts all bodies indifferently according to the same laws? No: chemical force is of a more complex nature. There is in it something which appears to be independent of the intensity itself. There is that elective action which was studied and defined by Bergman long before chemists had admitted the existence of those atoms of which it is an attribute. How does it happen that chlorine, which possesses so powerful an affinity for hydrogen, can annex to each of its atoms only a single atom of this body, whereas nitrogen can unite with three atoms of hydrogen? Why is phosphorus, which is so nearly allied to arsenic, and like the latter can unite with three atoms of hydrogen or three atoms of chlorine, capable of fixing as many as five atoms of chlorine in the perchloride of phosphorus? It is that the atoms of elementary bodies are not all made alike. Inde-

pendently of the differences in their relative masses and in their energies, we may suppose them to possess differences of form, movement, and structure, in consequence of which they are not capable of acting equally upon each other. This is doubtless one of the conditions which govern the elective actions of atoms and their unequal capacities of combination.

Here we return to the notion of atomicity; we meet with it again at the very foundation of the science, as one of the manifestations of chemical force. Each atom carries into its combinations two things: first its own proper energy; and secondly the faculty of expending this energy in its own way, in attaching other atoms to itself, not all indiscriminately, but certain atoms, and in definite numbers.

Atoms differ, then, not only by the force of their affinities, but by their combining capacities, by that power which they possess of selecting, to form those unions called compounds, a certain number of other atoms adapted to the peculiar nature of each. This is atomicity.

This fundamental property governs the forms of compounds, marks their degrees and their limits. It appears in the law of multiple proportions, shows itself in the fact of saturation, explains the functions of those incompletely saturated groups called radicals, and exhibits the fundamental meaning of the idea of types.

Why have we admitted a water-type?—because there exists a diatomic element, oxygen; and why does there exist an ammonia-type?—because there is a triatomic element, nitrogen.

We have already seen how this fundamental property of atoms is invoked in considerations relating to the atomic constitution of bodies: how the tendency of atoms to saturate themselves marks, as it were, the points of attachment of affinity, and indicates the mutual relations of atoms in compounds. To exhibit by a final development the grandeur and the wide scope of this notion of atomicity, we have still to show how it explains chemical reactions.

V.

Considered in a general point of view, and without reference to the phenomena of isomerism, these reactions may be included in one or other of the three following cases:

Formation of compounds by addition of atoms or of molecules.

Resolution of complex molecules into more simple elements.

Substitution in a compound of certain elements for others.

The dualistic system rested chiefly on the first two orders of chemical phenomena. Taking for its start-

ing point the ideas of Lavoisier upon salts, it represented all compounds as formed by addition of two elements ready to separate again. Dumas, relying on the phenomena of substitution, first regarded a chemical molecule as forming a complete whole, the different parts of which were united by affinity. Gerhardt adopted this idea. He moreover supposed that all chemical reactions take place between entire molecules by way of exchange between their elements. 'Everything is double decomposition.' Such is the formula by which he expressed all chemical transformations, exaggerating the point of view brought to light by the theory of substitution. We now know that he went too far in his reaction against ideas which had formerly been exaggerated by Berzelius.

All is not double decomposition: there are such things as fixation and abstraction of elements; there are molecules susceptible of increase by a direct addition of atoms; others again which can break up and resolve themselves into independent fragments.

All these reactions are explained by the notion of atomicity.

We know indeed the tendency of atoms to satisfy their combining capacities, and the law of multiples shows us that this tendency can be satisfied by degrees. Whenever any given compound contains a polyatomic element incompletely saturated, this com-

pound tends to attach to itself new atoms, in order to arrive at that state of saturation characterised by the interchange of all the atomicities.

We may thus distinguish in chemical compounds two different states: in saturated molecules, equilibrium of the atomicities; in incomplete molecules, instable equilibrium, and a deficit requiring to be filled up.

Why can olefiant gas fix two atoms of chlorine, like mercury or zinc, and thus play the part of a radical? Because the two atoms of carbon which it contains can, without ceasing to be united, each take up three monatomic elements, while in the gas itself each of them fixes only two atoms of hydrogen. Thus the molecule increases by this addition of two atoms of chlorine, and it then arrives at a state in which it is incapable of fixing any more atoms by direct combination. Does this amount to saying that the new molecule, which now constitutes chloride of ethylene, must in future be incapable of modification, that it has become indifferent, and, as it were, insensible to the action of other molecules? By no means. The chloride of ethylene can either break up, or exchange some of its elements for other elements. Let the chlorine which it contains be exposed to the action of powerful affinities: it will either separate purely and simply, or be replaced by other atoms. We must observe also that, in this latter case, each

atom of chlorine will be replaced by an element which will fulfil exactly the same function as itself in the new compound resulting from the substitution. This is equivalent to saying that the new element will be united by one atomicity to the atom of carbon, to which the above-mentioned chlorine atom in the chloride of ethylene was previously attached. If this new element is monatomic, like chlorine, the substitution will take place atom for atom, and the new compound will have the same molecular structure as the chloride of ethylene. In the contrary case, if the element substituted for the chlorine is polyatomic, it will carry into the new compound a number of atomicities larger than that which is required to satisfy those of one of the carbon atoms, as was done by the chlorine. Taking, then, the place of the latter, it will likewise draw into the compound other atoms capable of satisfying its still disengaged atomicities. The molecule will still increase, no longer by direct addition of new elements, but by the substitution of a group of atoms of a compound radical for a simple body.

It is thus that the theory of atomicity accounts for the functions of radicals, which in so large a number of reactions are substituted for elementary bodies; it is thus that it explains and enlarges the celebrated proposition enunciated by the first authors of the substitution theory, and applied in the first instance

to chlorine, namely, that elements which in compounds already formed are substituted for other elements, take the place and play the part of these latter.

They replace them by their capacity of combination; they place themselves in the new compound precisely in connection with the atom which in the old compound was saturated by the elements that have disappeared. Does this amount to saying that by such substitutions the properties of bodies ought not to suffer any modification? that the elements which have entered by substitution should replace those which have gone out in all their attributes? and that consequently it is indifferent, so far as properties are concerned, whether a compound contains hydrogen, chlorine, or oxygen, substituted one for the other, provided only that the substitution takes place in equivalent quantities according to the rule of atomicity? No; it is not thus that we must understand the function of elements in cases of substitution. If those of similar atomicity can replace each other with equal value so far as regards their capacity of combination, they cannot replace and balance one another with respect to their properties; for each of them brings into the combination its own proper nature, its energy, and its special affinities.

To account for the properties of compound bodies, a preponderating influence has by turns been attributed, either to the nature of the elements or to their

mode of grouping. It is more correct to say that the properties of bodies depend at once on these two conditions, each of which exerts considerable influence.

Considerations of this nature must be invoked to account for the properties, or, more properly speaking, the functions, which have most strongly attracted the attention of chemists: we allude to the acid and basic functions which show themselves in the neutralisation of acids by bases in the formation of salts. Why are certain bodies possessed of acid properties? 'Because,' said Lavoisier, 'they contain a large quantity of oxygen.' The reply was good, but not sufficient. We now know that the neutralisation of acids by bases takes place by exchange of the hydrogen of the one for the metal of the other, and that this hydrogen becomes ready for such exchange only when it is in connection with one or more elements possessed of strong electro-negative energy. An atom of chlorine, bromine, iodine, or even sulphur, is sufficient to bring the hydrogen into this peculiar state. Hydrochloric, hydrobromic, and hydriodic acids are powerful acids; sulphydric acid is a feeble acid. A single atom of oxygen is not sufficient to bring the hydrogen into the condition favourable to the exchange under consideration. This oxygen must be united with other elements, and sometimes with other atoms of oxygen, to render it capable of imparting the basic property, that is to say, the faculty of exchanging

itself for a metal, to the hydrogen placed in the neighbourhood of all these atoms. It is here that the notion of atomicity enters into the explanation of these fundamental reactions. Atoms assume particular properties by the contact and neighbourhood of other atoms, and their mutual relations, determined by considerations deduced from atomicity, exert a manifest influence on the properties of bodies. Let us take a single example to define this idea.

Hydrocarbons are formed, as already mentioned, of a chain of carbon atoms surrounded by hydrogen atoms. Suppose now one of these hydrogen atoms, belonging to a certain atom of carbon, to be replaced by the residue called oxhydryl, which consists of water less one atom of hydrogen: there will result from this substitution an alcohol, that is to say, a neutral body. The hydrogen of this residue does not exhibit any tendency to exchange itself for a metal. But when another atom of oxygen attaches itself to this residue, united, like itself, to the same atom of carbon, the hydrogen of the oxhydryl, now finding itself in the neighbourhood of two atoms of oxygen united with the same atom of carbon, will have changed its character or its function. In connection with a single oxygen atom, it was neutral; in the neighbourhood of two oxygen atoms it becomes basic.* In fact, all organic compounds

* Note 22, p. 209.

in which one of the carbon atoms is in connection with an oxygen atom and the group oxhydryl are acids; and we see that the acid function is here determined, not only by the nature of the atoms which are united, but likewise by their number and their mutual relations—by those relations, indeed, which are revealed to us by the notion of atomicity. We see also that if, to go to the root of the matter, we were to ask in what manner the properties of atoms are thus influenced by their mutual contact, and why these exchanges of hydrogen for a metal are so much facilitated in compounds in which this hydrogen is connected with one or more atoms endowed with great electro-negative energy, we should doubtless have to content ourselves with the reply that these reactions, these saturations of acids by bases, these interchanges of elements, are in reality connected with thermic phenomena.

Bodies, in acting on one another, expend, in the form of heat, a portion of their chemical energy, and the reactions of which we speak, like many others, proceed in a determinate direction, according to the greater quantity of heat evolved. It is the peculiar energy of the atoms, as manifested in their heat of combination, that comes into play in all these reactions; and when they are accomplished, the greatest possible quantity of energy has quitted the atoms in the form of heat, or, in other words, the

affinities have received the greatest possible satisfaction.

Is this all? Do all these mutual actions of acids and bases, which Lavoisier studied so deeply, making them the foundation of his system, range themselves in the order of facts just defined? and are they at bottom nothing but particular cases of the theory of substitution? It would be an error to think so, and it is proper to point out a particular case which may occur, and of which the advocates of the dualistic theory might avail themselves as an argument against the new theory.

Anhydrous acids can unite directly with anhydrous oxides to form salts. Does not carbonic acid gas unite directly with lime? and does not anhydrous sulphuric acid combine with barium oxide with such violence as to give rise to vivid incandescence? In this case there is no interchange of elements, no substitution of a metal for hydrogen: for the acid is anhydrous, and does not contain that element. This is true; but it must be observed that the saturation of barium oxide by sulphuric anhydride is a phenomenon of a different order from the neutralisation of barium hydrate by sulphuric acid. This latter reaction is a double decomposition or substitution, as above explained; the other results from the addition of elements, two molecules, both saturated, but formed of polyatomic elements, being riveted together in

consequence of an exchange of atomicities. In barium oxide the atom of barium and the atom of oxygen exchange all their atomicities; in barium sulphate they exchange only half; and the two atomicities which have become disposible, serve, as it were, to fix the elements of the sulphuric anhydride.* There is, therefore, an addition of atoms by displacement of atomicities; in other words, the atoms of the two bodies, in order to enter into combination, have changed their positions, and then joined themselves together in a certain manner; and this change of position, followed by an exchange of atomicities, has caused them to lose a portion of their energy: hence a disengagement of heat. Thus this particular case of the saturation of acids by oxides falls into the general line of reactions, which are foreseen and explained by the new theory of atomicity.

Here, then, we arrive at the end of this long exposition. Having taken up the doctrines of chemistry at their very birth, we have followed them through their successive evolutions. We have seen partial theories emerge and raise themselves against one another, then, after having fought, lend each other mutual aid, and subordinate themselves to a more general theory. We have seen the progress of ideas following closely on the march of discovery, and ar-

* Note 20, p. 208.

riving, through many variations, at the same fundamental idea, that, namely, which consists in seeking the first cause of chemical phenomena in the diversity of matter, each primordial substance being formed of atoms endowed with a certain energy, and with a peculiar aptitude for expending that energy. These two properties of atoms, distinct from one another, render an account of all chemical phenomena, the former measuring their intensity, the latter denoting their manner. Affinity and atomicity are, therefore, the two manifestations of the force which resides in the atoms, and this hypothesis of atoms forms at present the foundation of all our theories, the solid base of our system of chemical knowledge. It gives a striking simplicity to the laws relating to the composition of bodies; it enables us to look into their intimate structure; it intervenes in the interpretation of their properties, reactions, and transformations; and will doubtless at some future time furnish points of support for the science of molecular mechanics.

It was, therefore, a grand idea that was originated by Dalton, and it may with good reason be asserted, that amongst all the advances that chemical doctrines have made, since the time of Lavoisier, this is the most important; it has changed the face of the science: for the latest developments that have sprung from it have substituted for the old ideas on the mode of action of affinity, and on dualism in combi-

nation, a broader conception, which now includes, as particular cases, the reciprocal action of acids and bases on which the system of Lavoisier was founded. The dominant idea of that system, the dualistic constitution of salts, already questioned by great minds fifty years ago, is no longer acceptable at the present day, and the attempt to keep it up would be vain. Ought we to regret it for the sake of the teaching of the science, in which this theory, so beautiful in its simplicity, reigned undisputed for sixty years? We do not think so. The contrary hypothesis proposed by Davy and Dulong, and rendered triumphant by Laurent and Gerhardt, accounts for the facts with exactness and clearness, and embraces a greater number of them. As to Lavoisier, his glory remains in all its brightness. His work consists in his immortal discoveries, in his method, in the principles of eternal truth which he laid down on the nature of elementary bodies and on chemical combination, not on a formula relating to the composition of salts. The dualistic hypothesis employed by him to express that constitution, and extended by his successors to the whole range of chemistry, has had its day. To those who, from system or from habit, would still wish to retain it, seeking to shelter it under the great name of Lavoisier, we are tempted to recall the maxim of Bacon :—'Truth is the daughter of time, and not of authority.'

NOTES.*

Note 1, Page 25.

Lavoisier and Berthollet regarded hydrochloric (muriatic) acid as containing an unknown radical combined with oxygen. It is known that chlorine decomposes water in presence of light, with formation of hydrochloric acid and disengagement of oxygen. By this fact Berthollet was led to suppose that chlorine is a compound of muriatic acid and oxygen. He supposed that the unknown radical of muriatic acid can form with oxygen various compounds, namely:

With a small quantity of oxygen, muriatic acid.
With a larger quantity, oxymuriatic acid (chlorine).
With a still larger proportion, hyperoxymuriatic acid (the acid of chlorate of potash).

This theory was in accordance with the ideas of Lavoisier. It included the chlorides (muriates) in the class of oxygenated salts. It prevailed till 1810, when Davy showed that the simplest interpretation of the facts relating to the yellow gas discovered by Scheele consisted in regarding this gas as an elementary body, to which he gave the name of chlorine.

* The author's notes are distinguished by numbers; those added by the translator, by letters.

Note 2, Page 54.

In the formulæ of oxygenated compounds Berzelius contented himself with expressing the atoms of oxygen by superposed points. Thus he wrote

Sulphate of lead	$SO^3 + PbO$ or $\dddot{S}Pb$
Nitrate of potash . . .	$\ddot{N}O^5 + KO$ or $\ddot{N}\dot{K}$

In this notation we see clearly that the sulphate contains the elements of a sulphide plus 4 atoms of oxygen, of which 3 are attached to the sulphur and 1 to the metal. The ponderal relations between the metal and the sulphur are the same in a sulphide and a sulphate; this is as it should be, since the proportions by weight represent atoms whose weight is invariable. Berzelius proved this, thus verifying by experiment the consequences of the atomic theory, and giving to this theory a solid foundation by his numerous and exact analyses.

Note 3, Page 59.

To explain the function of ethyl as a radical, we here give the formulæ assigned by Berzelius to the ethylated compounds, placing side by side with them the corresponding compounds of a metal such as potassium. In these formulæ the barred letters represent double atoms:

Compounds of Ethyl	Compounds of Potassium
$C^4\bar{H}^5$ radical ethyl	K radical potassium
$C^4\bar{H}^5.\bar{C}l$ chloride of ethyl	$K\bar{C}l$ chloride of potassium
$C^4\bar{H}^5.O$ oxide of ethyl (ether)	KO oxide of potassium
$C^4\bar{H}^5.O + \bar{H}O$ hydrate of oxide of ethyl (alcohol)	$KO + \bar{H}O$ hydrate of oxide of potassium (caustic potash)
$C^4\bar{H}^5.O + C^4\bar{H}^3O^3$ acetate of oxide of ethyl (acetic ether)	$KO + C^4\bar{H}^3O^3$ acetate of oxide of potassium

Note 4, Page 63.

The celebrated hypothesis of benzoyl, due to Wöhler and Liebig, marks a considerable progress in the radical theory. The following formulæ, borrowed from the notation of Berzelius, may serve to throw light upon it:

$C^{14}H^{5}O^{2}$ benzoyl
$C^{14}H^{5}O^{2}.H$ hydride of benzoyl (bitter almond oil)
$C^{14}H^{5}O^{2}.Cl$ chloride of benzoyl
$C^{14}H^{5}O^{2}.O$ oxide of benzoyl (anhydrous benzoic acid)
$C^{14}H^{5}O^{2}.S$ sulphide of benzoyl
$C^{14}H^{5}O^{2}.O + HO$ hydrate of oxide of benzoyl (hydrated benzoic acid)
$C^{14}H^{5}O^{2}.O + KO$ benzoate of potash

Note 5, Page 70.

Berzelius, and all the partisans of Lavoisier's theory of salts, supposed that hydrated acids contain the elements of anhydrous acids, together with the elements of water, and that salts contain the elements of an anhydrous acid together with the elements of an oxide. Thus, in the notation of Berzelius, sulphuric acid and the sulphates of potash and lead were represented by the following formulæ:

Sulphuric acid or Sulphate of water . .	$SO^{3} + H^{2}O$
Sulphate of potash	$SO^{3} + KO$
Sulphate of lead	$SO^{3} + PbO$

This notation shows that the elements of water, oxide of potassium, and oxide of lead are simply added to the elements of the anhydrous acid without being mixed up with them.

Longchamp supposed, on the contrary, that this oxide removes an atom of oxygen from the anhydrous acid, being thereby converted into a peroxide, which remains united to

the deoxygenated acid. Thus, he represented the constitution of the preceding compounds by the following formulæ:

Sulphuric acid . . .	$SO^2 + H^2O^2$
Sulphate of potash . . .	$SO^2 + KO^2$
Sulphate of lead . . .	$SO^2 + PbO^2$

The formula $SO^2 + PbO^2$ was based on the fact of the formation of sulphate of lead by the action of sulphurous acid gas on peroxide of lead.

We now know that the two atoms of hydrogen in sulphuric acid,

$$SO^4H^2 = SO^2.O^2H^2$$

are each in connection with an atom of oxygen, and that these two atoms of oxygen discharge a function different from that of the other two, which are contained in the radical sulphuryl SO^2. This radical is diatomic; it combines with 2 atoms of chlorine, and the resulting chloride of sulphuryl, by reacting with water, forms sulphuric acid.

$SO^2\{^{Cl}_{Cl}$ — Chloride of sulphuryl

$SO^2\{^{OH}_{OH}$ — Sulphuric acid

Sulphuric acid appears then like a compound of sulphuryl with two groups of OH or oxhydryl. Longchamp regarded it as sulphurous gas (sulphuryl) combined with oxygenated water, O^2H^2. These two modes of viewing the compound are certainly different, but it must be admitted that they have a point of contact. To be convinced of this, it is sufficient to cast the eye over the atomic formulæ of the sulphates, which are almost identical with those of Longchamp:

Sulphuric acid	$SO^2.O^2H^2$
Potassium sulphate . . .	$SO^2.O^2K^2$
Lead sulphate	$SO^2.O^2Pb''$

Note 6, Page 78.

We have observed that Berzelius regarded acetic acid and its analogues as oxides of hydrocarbon-radicals, combined with the elements of water. Acetic acid was the hydrate of the trioxide of acetyl. As to trichloracetic acid, he regarded it as a conjugated compound of oxalic acid and chloride of carbon, united to the elements of water. We see then that acids, between which the substitution theory pointed out relations of so much simplicity, were, for Berzelius, compounds of very different orders. These divergences are exhibited by the following formulæ:

	Substitution formulæ	Formulæ of Berzelius
Acetic acid . .	$C^4H^3O^3.HO$	$C^4H^3.O^3 + HO$
Trichloracetic acid .	$C^4Cl^3O^3.HO$	$C^2O^3.C^2Cl^3 + HO$

We will cite a few more examples to give an idea of the complexity of dualistic formulæ. Malaguti's perchloric ether was regarded as a double compound of 1 molecule of anhydrous oxalic acid with 5 molecules of oxalic chloride (sesquichloride of carbon). Berzelius designated this compound as *oxal-aci-quintichloride*. Malaguti's perchlorinated oxalic ether becomes a compound of 4 atoms of oxalic acid and 5 atoms of sesquichloride of carbon; Berzelius calls it *oxal-quadraci-quintichloride*, and thinks that it may be regarded as containing 3 molecules of oxal-acichloride united to 1 atom of oxal-aci-bichloride. The following formulæ express these singular conceptions:

Ether . . .	C^4H^5O	C^4H^5O
Perchlorinated ether	C^4Cl^5O	$C^2O^3 + 5C^2Cl^3$ oxal-aci-quintichloride
Oxalic ether .	$C^2O^3.C^4H^5O$	$C^2O^3 + C^4H^5.O$
Perchlorinated oxalic ether . .	$C^2O^3.C^4Cl^5O$	$4C^2O^3 + 5C^2Cl^3$ oxal-quadraci-quintichloride $= 3[C^2O^3 + C^2Cl^3] + [C^2O^3 + 2C^2Cl^3]$

Note 7, Page 81.

The following are the terms in which Dumas discusses the opinion which consisted in regarding the theory of substitution as a particular case of the theory of equivalents.

'Berzelius is willing to accept these facts as doubtless a particular case of the theory of substitutions. In this respect he shares an opinion frequently advanced in Germany, which I have never thought it necessary to refute, namely, that the theory of equivalents was sufficient to teach us that hydrogen could be replaced by its equivalent of chlorine or of oxygen. I cannot say who was the first to make use of this objection against the theory of substitution, but I have never believed that it would make any impression on the minds of chemists. Is it not evident, indeed, that if a body contains, for example, 8 volumes of hydrogen, the theory of equivalents will be satisfied if chlorine has removed without replacing them; that it will be no less satisfied if they are found to have disappeared, and that 2, 4, 6, or 8 volumes of chlorine have remained in their place, or, even, 10, 12 or 20 volumes of this gas? in a word, provided that the quantities of chlorine and of hydrogen which the compound loses or retains may be expressed by any equivalents whatever, the theory of equivalents would be satisfied therewith. It is not thus with metalepsy.' . . .

Note 8, Page 82.

Berzelius, having at first regarded trichloracetic acid as a copulated compound of oxalic acid and sesquichloride of carbon, afterwards extended this hypothesis to acetic acid itself, supposing that this acid contains as copula the group C^2H^3:

Trichloracetic acid . . .	$C^2Cl^3.C^2O^3 + HO$
Acetic acid	$C^2H^3.C^2O^3 + HO$

Note 9, Page 85.

In a memoir on the chlorides of naphthalene (*Annales de Chimie et de Physique*, 2me sér., t. lii. p. 275, 1833), Laurent describes two compounds of naphthalene—a solid chloride, $Ch^2 + C^{10}H^3$, and an oily chloride, to which he attributes a more complicated composition. This is how he expresses himself with regard to the solid chloride (p. 281): 'By the formula $Ch^2 + C^{10}H^3$ one might give the theory of the formation of this compound by saying that 3 volumes of chlorine acting on 1 volume of naphthalene, $C^{10}H^4$, convert it into a peculiar chloride, $Ch^2 + C^{10}H^3$, and evolve 2 volumes of hydrochloric acid. The body $Ch^2 + C^{10}H^3$ is therefore the solid chloride of a peculiar hydrocarbon.'

Note 10, Page 114.

The following formulæ express the relations of composition existing between ammonia and the ethylated ammonias:

$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}C^2H^5\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right.$	$N\left\{\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right.$
Ammonia	Ethylamine	Diethylamine	Triethylamine

Note 11, Pages 116 and 126.

The following formulæ represent Williamson's ideas on the constitution of acids, oxides, and salts referred to that of water:

$\left.\begin{matrix}H\\H\end{matrix}\right\}O$ water	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$ water	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$ water
$\left.\begin{matrix}H\\K\end{matrix}\right\}O$ hydrate of potassium	$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$ alcohol	$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$ acetic acid
$\left.\begin{matrix}K\\K\end{matrix}\right\}O$ oxide of potassium	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O$ ether	$\left.\begin{matrix}C^2H^3O\\K\end{matrix}\right\}O$ acetate of potassium
$\left.\begin{matrix}NO^2\\K\end{matrix}\right\}O$ nitrate of potassium	$\left.\begin{matrix}C^2H^5\\C^2H^3O\end{matrix}\right\}O$ acetic ether	$\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O$ acetic anhydride

Note 12, Page 122.

In their memoir on the amides (*Comptes rendus*, t. xxxvii. p. 86), Gerhardt and Chiozza have described primary, secondary, and tertiary amides formed by substitution of 1, 2, and 3 acid radicals for 1, 2, and 3 atoms of hydrogen in ammonia:

Primary amide	Secondary amide	Tertiary amide
$\left.\begin{matrix} C^7H^5O \\ H \\ H \end{matrix}\right\} N$	$\left.\begin{matrix} C^7H^5O \\ C^7H^5O^2 \\ H \end{matrix}\right\} N$	$\left.\begin{matrix} C^6H^5SO^2 \\ C^7H^5O \\ C^7H^5O \end{matrix}\right\} N$
Benzamide	Benzoyl-salicyl-amide	Dibenzoyl-sulpho-plenamide

They observe that the secondary amide, benzoyl-salicyl-amide, in alcoholic solution, reddens litmus, and easily exchanges 1 atom of hydrogen for 1 atom of metal, like an acid properly so called.

Note 13, Pages 120 and 122.

Bodies of similar constitution are brought together, but not confused, by the theory of types. The properties of bodies must necessarily vary according to the nature of the elements which they contain, and may even pass from one extreme to the other. This contrast is fully borne out by the antagonism of the elements themselves. This is shown by the following table:

Left or Positive Extremity	Intermediate Terms	Right or Negative Extremity
$\left.\begin{matrix} K \\ H \end{matrix}\right\} O$ hydrate of potassium	$\left.\begin{matrix} H \\ H \end{matrix}\right\} O$ hydrate of hydrogen (water)	$\left.\begin{matrix} Cl \\ H \end{matrix}\right\} O$ hydrate of chlorine or hypochlorous acid
$\left.\begin{matrix} Na \\ H \end{matrix}\right\} O$ hydrate of sodium	$\left.\begin{matrix} C^2H^5 \\ H \end{matrix}\right\} O$ hydrate of ethyl (alcohol)	$\left.\begin{matrix} C^2H^3O \\ H \end{matrix}\right\} O$ hydrate of acetyl (acetic acid)

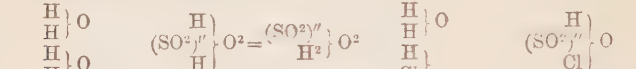
According to Gerhardt's idea, bodies constituted in the same manner are here arranged on the same horizontal line. Alcohol is here regarded, not as alkaline and analogous to

hydrate of potassium, but rather as analogous to water, as regards its neutrality. In a table published in 1852, and reproduced in the memoir on anhydrous organic acids, Gerhardt had placed alcohol at the left or posterior extremity. On account of its historic importance we think it advisable to reproduce this table.

	Left or Positive Extremity	Intermediate Terms	Right or Negative Extremity
Water type $\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$ alcohol	. . .	$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$ acetic acid
	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}O$ ether	. . .	$\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O$ anhydrous acetic acid
	$\left.\begin{matrix}CH^3\\C^2H^5\end{matrix}\right\}O$ methylic ether	. . .	$\left.\begin{matrix}C^2H^3O\\C^7H^5O\end{matrix}\right\}O$ benzoic acetate
	. . .	$\left.\begin{matrix}C^2H^5\\C^2H^3O\end{matrix}\right\}O$ acetic ether	. . .
Hydrogen type $\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}$ hydride of ethyl	. . .	$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}$ aldehyde
	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}$ ethyl .	. . .	$\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}$ acetyl
	. . .	$\left.\begin{matrix}CH^3\\C^2H^3O\end{matrix}\right\}$ acetone	. . .
Hydrochlor. acid type $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}$ hydrochloric ether	. . .	$\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}$ chloride of acetyl
Ammonia type $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}N$ ethylamine	. . .	$\left.\begin{matrix}C^2H^3\\H\\H\end{matrix}\right\}N$ acetamide
	$\left.\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right\}N$ diethylamine	. . .	. . .
	$\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}N$ triethylamine	. . .	. . .

Note 14, Page 130.

The following formulæ explain the idea of condensed and mixed types, and the functions of polyatomic radicals in compounds referred to these types:



2 molecules of water (condensed type) — 1 molecule of sulphuric acid — 1 mol. water and 1 mol. hydrochlor. acid (mixed type) — Chlorosulphuric acid

Note 15, Page 134.

According to the system of atomic weights which he had adopted in 1815, Berzelius at first regarded ferric oxide and alumina as containing 1 atom of metal and 3 atoms of oxygen. Afterwards (1826) he modified this opinion, assigning to iron and aluminium smaller atomic weights, and to their oxides the formulæ Fe^2O^3 and Al^2O^3, which are still in use.

Note 16, Page 137.

The following formulæ represent the composition of phosphoric acid in equivalents; the atomic formulæ are also given for the sake of comparison:

	Equivalent formulæ	Atomic formulæ
Phosphoric acid . . .	$PO^5,3HO$	H^3PO^4
Pyrophosphoric acid . .	$PO^5,2HO$	$H^4P^2O^7$
Metaphosphoric acid . .	PO^5,HO	HPO^3

Note 17, Page 145.

The word *polyatomic* was scarcely used before the time when Wurtz's first note, 'Sur le glycol ou alcool diatomique,'

was published, although it was not absolutely new. In a memoir published in 1845 (*Annales de Chimie et de Physique*, 3me sér. t. xiii. p. 142), M. Millon had established a distinction, on the one hand between monatomic and polyatomic bases, on the other between monatomic and polyatomic acids, these latter likewise resulting from the union of several molecules of greater simplicity. I may add that M. Malaguti, in his excellent *Leçons élémentaires de Chimie*, 1853 (p. 331), had substituted the denominations of monatomic, diatomic and triatomic acids for the more generally used terms, monobasic, bibasic and tribasic acids.

Note 18, Page 146.

The following formulæ explain the formation of glycol, and the idea enunciated by Wurtz concerning the functions of the radical ethylene:

$$\underset{\text{Ethylene iodide}}{(C^2H^4)''I^2} + \underset{\text{2 molecules of silver acetate}}{\begin{matrix} C^2H^3O \\ Ag \end{matrix}\Big\}O \quad \begin{matrix} Ag \\ C^2H^3O \end{matrix}\Big\}O} = \underset{\text{Silver iodide}}{2AgI} + \underset{\text{1 molecule of ethylene acetate}}{\begin{matrix} C^2H^3O \\ (C^2H^4)'' \\ C^2H^3O \end{matrix}\Big\}O^2}$$

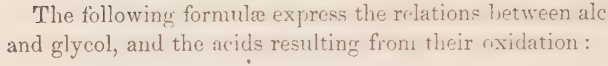
We see that the two molecules of silver acetate, losing 2 atoms of silver, take in their place the diatomic and indivisible radical ethylene, and are thus riveted together into a single molecule of ethylene-diacetate.

This latter compound, treated with potash, yields glycol:

$$\underset{\text{Ethylene diacetate}}{\begin{matrix} C^2H^3O \\ (C^2H^4)'' \\ C^2H^3O \end{matrix}\Big\}O^2} + \underset{\text{2 mol. of potash}}{\begin{matrix} H \\ K \end{matrix}\Big\}O \quad \begin{matrix} H \\ K \end{matrix}\Big\}O} = \underset{\text{Ethylene dihydrate (glycol)}}{\begin{matrix} H \\ (C^2H^4)'' \\ H \end{matrix}\Big\}O^2} + 2\underset{\text{2 mol. potassium acetate}}{\left[\begin{matrix} C^2H^3O \\ K \end{matrix}\Big\}O\right]}$$

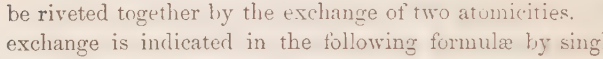
Note 19, Page 147.

The following formulæ express the relations between alcohol and glycol, and the acids resulting from their oxidation:



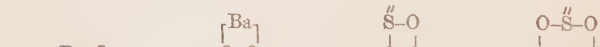
Note 20, Pages 161 and 193.

Free oxygen is formed of two atoms of oxygen, supposed to be riveted together by the exchange of two atomicities. This exchange is indicated in the following formulæ by single or double connecting bonds:



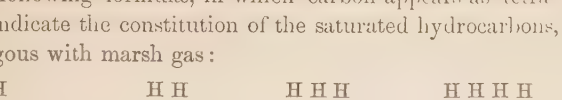
We here see that the oxygen-atoms can link themselves together to form a chain, at the extremities of which a single free atomicity is satisfied by a monatomic element, such as chlorine or hydrogen. This is what is called an open chain.

The chain may be closed when all the polyatomic elements which form it are soldered together. This is the case in certain peroxides, and in all probability in sulphuric anhydride, barium sulphate, &c.



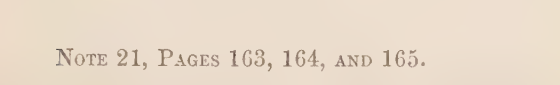
In this kind of notation, the atomicity of an element is reckoned by the number of connecting bonds which surround its symbol in the formula.

The following formulæ, in which carbon appears as tetratomic, indicate the constitution of the saturated hydrocarbons, homologous with marsh gas:



Note 21, Pages 163, 164, and 165.

The following formulæ indicate the relations between the atoms in the derivatives of ethyl hydride:



Note 22, Page 190.

The substitution of the group OH (oxhydryl or hydroxyl) for one atom of hydrogen in a hydrocarbon produces an alcohol; that of an atom of oxygen and of an oxhydryl group for three atoms of hydrogen produces an acid. An acid is, therefore, a body containing one or several groups of CO^2H (carboxyl or oxatyl).

Note A, Page 1.

The statement that chemistry, as a science, was founded by Lavoisier, requires some qualification. The first great generalisation of the facts of chemistry was, undoubtedly, the phlogistic theory of Stahl. Now, this theory took no account of the relations of weight between a combustible body and the products of its combustion, directing attention exclusively to the visible phenomena, the evolution of light and heat, attending the process; and it was, perhaps, by a natural reaction that, when the real nature of the change, and the great importance of the increase of weight experienced by the burning body, had been brought to light by the discoveries of Lavoisier, the attention of chemists should, for a considerable time, have been chiefly directed to these ponderal relations, and that even the good and valuable points in the phlogistic theory should have been, for the most part, overlooked.

But on viewing these phenomena by the light of recent investigations, it must be admitted that the thermal changes attending the process of combustion are quite as important as the ponderal changes. Indeed, as Dr. Crum Brown * has observed, in an ingenious paper on the phlogistic theory, a combustible body does actually, as the phlogistic chemists asserted, lose something in burning; and this something, which they called phlogiston, we now know to be the power of emitting a certain quantity of heat, or, in other words, a certain amount of potential energy. The importance of this change in the thermal condition of a burning body did not escape the sagacity of Lavoisier, who, indeed, speaks with admiration of the great discovery of Stahl, that the property of burning, that is, of being inflammable, may be transferred from one body to another; as when vitriolic acid, an incombustible body, is

* Proceedings of the Royal Society of Edinburgh, vol. v. p. 328.

converted into combustible sulphur by contact with charcoal, which is itself a combustible body, the charcoal at the same time becoming incombustible.* Lavoisier himself regarded vital air, or oxygen gas, as a compound of a ponderable base, called *oxygen*, with the imponderable element *caloric*, or *heat*, and supposed that in the process of combustion the ponderable oxygen unites with the combustible body, while the caloric is set free. He further regarded all elementary bodies as compounds of ponderable bases with caloric, the same body being supposed to contain more of that imponderable element in the liquid than in the solid state, and still more when in the state of gas. In accordance with these views he observes that greater heat is evolved in the combustion of hydrogen gas than in that of phosphorus, because, in the former case, a large quantity of caloric is given off by the combustible gas, as well as by the oxygen gas; and that less heat is evolved in the combustion of charcoal, because the product of this combustion is carbonic acid gas, or fixed air, which retains a certain quantity of caloric to keep it in the gaseous state.†

According to this theory, the evolution of heat in combustion is attributed mainly to the liberation of the latent heat, which retains a body in the gaseous state. But the insufficiency of this mode of explanation soon became apparent, when it was observed that great heat may be evolved in cases of combustion, where no condensation of a gaseous body to the liquid or solid state takes place, as in the combination of sulphur with copper or iron; and even when gaseous products are formed from solid bodies, as in the explosion of gunpowder

* Œuvres de Lavoisier, publiées par les soins de Son Excellence le Ministre de l'Instruction publique et des Cultes, Paris, 1862, tome ii. p. 625.

† Méthode de Nomenclature chimique, par MM. de Morveau, Lavoisier, Berthollet et de Fourcroy, Paris, 1787, p. 296.

or fulminating silver. To meet the necessities of these and similar cases various theories of combustion were from time to time proposed,* in particular the electro-chemical theory of Davy and Berzelius (p. 64), which attributed the heat and light evolved in combustion to the combination of the opposite electricities supposed to reside in the atoms of the combining bodies. This theory, however, like the others above alluded to, was never reduced to quantitative expression: and, indeed, it is only of late years that, by the researches of Favre and Silbermann, Andrews, and others, the quantities of heat evolved in various forms of chemical action have been determined with sufficient accuracy to be made the foundation of any exact theory of the phenomena.

The most general result yet arrived at, respecting the thermal phenomena of chemical action, is that the evolution or absorption of heat in any given reaction depends upon the relative stability of the system before and after that reaction. This subject has been treated with remarkable clearness by Dr. Odling, in a lecture on 'Reverse Chemical Action,' recently delivered at the meeting of the British Association at Norwich. In this discourse, it is shown that the passage from a less stable to a more stable arrangement of matter is always attended with evolution of heat, whether the said change be what is commonly called combination, or what is called decomposition. Thus, not only is heat evolved in the combustion of zinc or phosphorus in oxygen, or in the combination of phosphorus with iodine, but likewise in the decomposition of iodide of nitrogen, or of gun-cotton. These and other instances of direct chemical action, that is, of action taking place spontaneously as soon as the acting substances are brought under certain conditions of temperature, &c., may be compared to the falling of a weight to the ground as soon as the support which keeps it up is removed. In the

* See Gmelin's *Handbook of Chemistry*, English edition, vol. ii. p. 36.

one case we have an unstable mechanical equilibrium, the conversion of which into a more stable equilibrium is attended with a certain expenditure of actual motion; in the other, we observe that the conversion of an unstable chemical equilibrium into a stable chemical equilibrium is attended with an expenditure of heat, which is interstitial motion. Now just as to reverse the mechanical change above mentioned, that is, to lift a weight from the ground, a certain degree of mechanical force must be expended; so likewise to undo a direct chemical action—as, for example, to separate hydrogen from its combination with oxygen, or, in other words, to *unburn* it, a certain amount of heat, or its equivalent in mechanical or some other form of force, must be expended—the potential energy (the phlogiston of the old theory) which the bodies have lost by combination must be restored.

When hydrogen combines with oxygen to form water, there are evolved, for every 2 grammes of hydrogen combined with 16 grammes of oxygen, 68 units of heat;* and in order to separate or unburn the hydrogen, these 68 units of heat must be restored. This may be effected by burning or oxidising a more calorifacient substance, such as zinc, in contact with the water. When zinc burns in the air or in oxygen gas, for every 65 grammes of zinc which enter into combination with 16 grammes of oxygen, 86 units of heat are evolved. Now when zinc is acted upon by acidulated water, it dissolves, and is oxidised at the expense of the hydrogen, which is set free as gas; and this unburning of the hydrogen is attended with the evolution of a considerable quantity of heat, namely of 18 heat-units, which is the difference between the 86 units that would be evolved by the direct combustion of the zinc, and the 68 units which constitute the potential heat of the escaping hydrogen. This action may be compared with the

* The unit of heat is the quantity required to raise the temperature of one kilogramme of water, by 1° Centigrade.

lifting up of a weight by means of a heavier weight connected with the former by a string passing over a pulley, the falling motion of the heavier weight being diminished by the potential falling motion transferred to the lighter one. The unburning of the hydrogen might also be effected by the application of muscular effort to the handle of a magneto-electric machine, the current of which, when passed through water, will effect the separation of the oxygen and hydrogen. In this case the actual motion, which might be produced by the muscular effort expended, is diminished by the potential energy, or quasi-motion, of the separated hydrogen.

But the most direct method of effecting the unburning of the hydrogen consists in exposing water to a very high temperature, as by bringing it in contact with white-hot platinum, a mode of decomposition discovered about twenty years ago by Mr. W. R. Grove. When vapour of water is passed through a coil of platinum tube intensely heated by the flame of the oxyhydrogen blow-pipe, it is resolved into oxygen and hydrogen gases, which escape at the open end of the coil, and may be collected over water. Here we may say that the molecular motion generated by the burning of the hydrogen outside the tube is directly transferred to another portion of hydrogen, previously in combination with oxygen, and effects its separation.

In all such cases, the process of separation, or unburning, requires that the elements which separate shall be supplied with a quantity of heat or potential energy equal to that which they have lost by the act of combination or combustion — truly a very near approach to the language of the phlogistic theory. The exact study of these relations may be said to be in its infancy, on account of the great difficulty of obtaining precise experimental data respecting the quantities of heat evolved in chemical reactions; but it opens out a wide field of discovery, and will doubtless occupy a very prominent place in the chemistry of the future.

Note B, Pages 9 and 11.

Among the investigations belonging to the epoch immediately preceding Lavoisier, there is one which stands out in marked contrast to the rest, with regard both to the manner in which it was conducted, and the important influence which it exerted on the subsequent development of the science. This is the investigation, by Dr. Black, of Edinburgh, of the difference between mild and caustic alkalis—a research which may be regarded as the inauguration of the quantitative method in chemistry, and as the first instance in which the nature of chemical combination and decomposition was clearly pointed out.

The mild alkalis (carbonates) were at that time regarded as simple substances, which became caustic by combination with a so-called fiery matter; lime was also supposed to take up this same fiery matter in the process of burning, and to be capable of transferring it to other alkalis. This hypothesis further explained the fact that lime, after having been used to render a mild alkali caustic, is no longer itself caustic, having transferred its own fiery matter to the alkali.

Black appears, in the first instance, to have shared these notions; but having found by observation that caustic lime, when exposed for some time to the air, became heavier at the same time that it lost its causticity, instead of becoming lighter, as might have been expected if the change were really due to the escape of the supposed fiery matter, he perceived in this fact sufficient ground for rejecting the received doctrine of a ponderable caloric or fiery substance. He next ascertained that the loss of causticity and increase of weight were accompanied by a considerable absorption of air. On extending these observations to magnesia, he found that ordinary magnesia (magnesia alba) effervesced with acids; that it lost weight by ignition, and then no longer effervesced with acids,

though it still yielded with acids the same salts as the magnesia that had not been ignited. He then sought to ascertain what was separated from the magnesia by ignition, and with that view he heated a weighed quantity in a retort. Some water was thus obtained, but not sufficient to account for the whole loss of weight by the magnesia. This led him to suspect that air was disengaged from the magnesia by ignition; and to determine this point, he dissolved a known weight of ignited magnesia in sulphuric acid, and precipitated it by means of a mild alkali (carbonate of potash): whereupon, after washing and drying the precipitate, he found that it had increased in weight as much as the magnesia had lost in weight by ignition, and that it had recovered the power of effervescing with acids, and all the other properties which the magnesia had lost by ignition. Hence he concluded that the loss of weight and alteration of qualities presented by magnesia on ignition were due to the separation of air, and that the restitution of those qualities, and the increase of weight when ignited magnesia was dissolved in acid and precipitated by a mild alkali, were due to its recovery from the alkali of the air that had been expelled by ignition. In this latter conclusion he was guided by a previous observation made by Hales, that fixed alkali contains abundance of air. He then examined the gas eliminated by acids from mild alkalis, or lime, or magnesia alba, and collected it in a vessel. He named this gas 'fixed air,' and soon afterwards showed that it is identical with the gas evolved in fermentation.

Thus was Black led to the conclusion that effervescing earths and alkalis contain, as one of their essential constituents, a gas which can be expelled by heat from the former, but not from the latter—from both, however, by acids; that the alkalis and earths, when freed from this gas, become caustic, and, therefore, that their causticity does not depend on the presence of a peculiar substance, but belongs to them in their perfectly

pure state; that they are made caustic by the separation of this fixed air; and that caustic lime renders mild alkalis caustic, not by imparting to them any caustic or fiery principle, but by abstracting the fixed air which they contain. He further observed that this gas or air, to a certain extent, neutralises the alkalis, that is to say, weakens their caustic properties in combining with them.

On reviewing this admirable investigation, we see plainly that the difference between Black's explanation of the relation between mild and caustic alkalis, and that which attributed their diverse qualities to the presence or absence of fiery matter, is precisely analogous to the difference between the explanations of the phenomena of combustion afforded by the phlogistic and antiphlogistic theories. It is true that Black himself did not perceive this analogy; that is to say, he did not perceive that the change which a metal, for example, undergoes in calcination, consists, like the conversion of a caustic into a mild alkali, in its combination with a ponderable substance—the fixation of a kind of air. Having been educated in the ideas of the phlogistic school, he maintained the doctrines of that school, so far as the phenomena of combustion were concerned, during the greater part of his career, though he ultimately became a convert to Lavoisier's views; but there can be no doubt that his investigation of the difference between mild and caustic alkalis was the first that showed the importance of quantitative relations in the interpretation of chemical phenomena; and that his demonstration that the conversion of a mild into a caustic alkali, or the contrary, is due to the abstraction or addition of a ponderable substance (carbonic acid), was the inauguration of those ideas of chemical combination and decomposition, which were afterwards extended by Lavoisier to the whole range of chemical phenomena.

Note C, Page 91.

Isomorphism.—Intimately related to the law of substitutions, is the important fact, discovered by Mitscherlich, that bodies having a similar chemical constitution have also the same crystalline form, as determined by the measurement of their angles—or, in other words, that analogous elements and groups of elements may replace one another in composition without essential alteration of crystalline form. Mitscherlich's first observations, communicated to the Berlin Academy of Sciences in 1819, related to the phosphates and arsenates, and showed that these salts, when they contain the same base, united with equivalent quantities of phosphoric and arsenic acids, and are further united with equal numbers of molecules of crystallisation-water, exhibit perfectly identical crystalline forms, agreeing with one another even in the secondary modifications. He established this fact for the most various salts of those acids containing potassium, sodium, ammonium, barium, lead, &c.; and likewise for their double salts containing potassium and ammonium, and thence concluded that the elements arsenic and phosphorus are capable of replacing one another, atom for atom, without alteration in the crystalline form of the resulting compounds. Bodies thus related to one another were designated by Mitscherlich as isomorphous bodies (*ἰσόμορφος*, similarly shaped).

This law, that compounds containing isomorphous elements, and similar to one another in atomic constitution, always exhibit similar crystalline forms, was soon afterwards demonstrated by Mitscherlich for a large number of other compounds. He showed that nickel oxide, zinc oxide, and magnesia, neutralised with sulphuric acid, and combined with equal numbers of molecules of water, likewise form salts identical in crystalline form, and that the same law holds good for the cobaltous

and ferrous salts. From the fact that the protoxides of calcium, magnesium, zinc, manganese, and iron, in combination with carbonic acid, crystallise without essential difference of form, Mitscherlich concluded that these bases are isomorphous, and that their compounds with sulphuric acid, for example, should also crystallise in similar forms; he found, indeed, that such is always the case, excepting when the atomic constitution of the salts is altered by combination with different quantities of water. Mitscherlich likewise showed, as, indeed, had been previously pointed out by Leblanc and Beudant, that when two such salts (e.g. ferrous sulphate and zinc sulphate) of different crystalline forms (and containing unequal quantities of water) crystallise together, and take the form peculiar to one of them, the other salt likewise takes up the same quantity of water as the former; so that in a complex salt of this nature, the two component salts have the same atomic constitution, although, when they crystallise separately, they may differ in their amounts of water of crystallisation. He further showed that all these salts, when they combine with the neutral sulphate of potash or ammonia, form double salts resembling one another exactly in atomic constitution and crystalline form. Another remarkable case of isomorphism, subsequently established by Mitscherlich, was that of the corresponding salts of sulphuric and selenic acids, from which it was inferred that sulphur and selenium are isomorphous elements, and form compounds of similar atomic constitutions.

In this manner Mitscherlich demonstrated the existence of groups of isomorphous bodies, that is, of bodies which, when united in similar atomic proportions with a third, of any constitution whatsoever, produce compounds similar in crystalline form. He established, in fact, the 'law of isomorphism,' which since the year 1820, in which it became generally known, has been received as one of the most important generalisations of theoretical chemistry. It has afforded valuable

assistance in the classification of the elementary bodies, and in the determination of the atomic constitution of compounds, and consequently in the numerical estimation of atomic weights, as in the well-known instance of aluminium, which was inferred to form a sesquioxide Al^2O^3, and corresponding salts, from the isomorphism of the alumina compounds with the corresponding compounds of ferric oxide, Fe^2O^3. A more recent and very remarkable instance of this application of the law of isomorphism is afforded by Professor Roscoe's researches on vanadium. This metal was formerly supposed to form compounds analogous to those of chromium and tungsten, its highest oxide being regarded as a trioxide VO_3, analogous to anhydrous chromic and tungstic acids. But, guided by the isomorphism of the vanadates with the phosphates and arsenates, Roscoe has succeeded, by a careful and elaborate examination of the vanadium compounds, in showing that this metal is a pentad: that the formula of anhydrous vanadic acid is V^2O^5, and that the vanadates are analogous in composition, as well as similar in form, to the phosphates and arsenates.

In connection with this subject, however, it must be observed that isomorphism between the corresponding compounds of two elements must not be supposed to afford a perfectly sure indication that those elements are of equal atomicity, for Marignac has shown that the nioboxyfluorides are isomorphous with the stannofluorides, titanofluorides, and tungstofluorides, whereas niobium is a pentad, tin and titanium are tetrads, and tungsten is a hexad. Generally, it may be said that similarity of atomic constitution between compounds of isomorphous elements, necessarily produces similarity of form, but that this latter relation may likewise exist, and often does exist, between compounds not similar to one another in atomic constitution.

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